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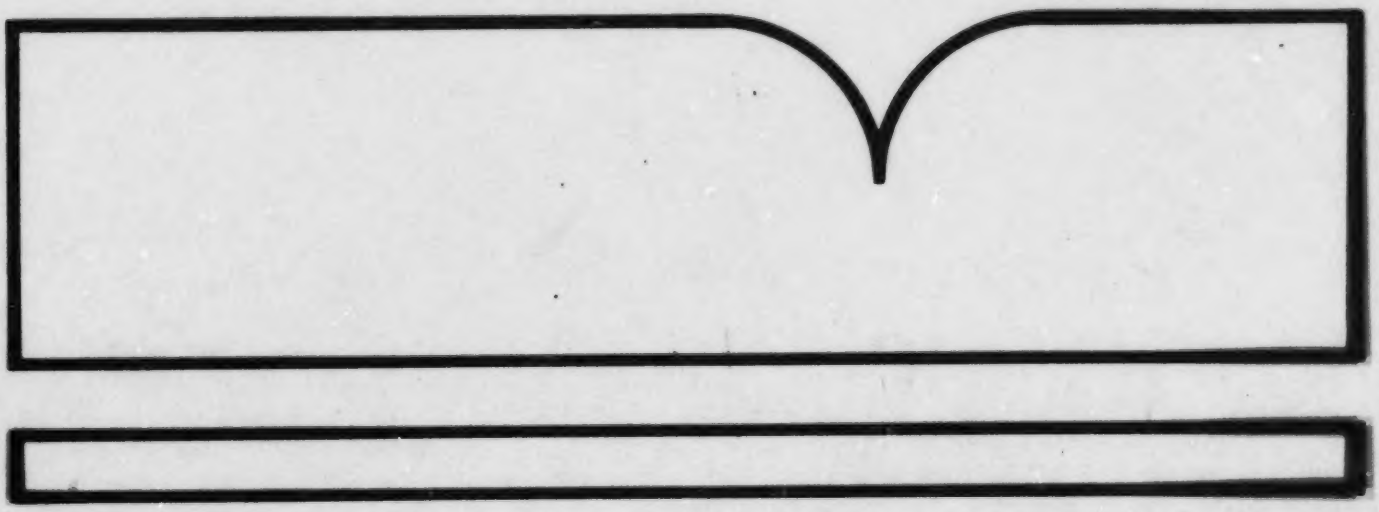
Static Coal Storage - Chemical Effects on The Aquatic Environment

Wisconsin Univ.-Superior

Prepared for

Environmental Research Lab.
Duluth, MN

Aug 80



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16. ABSTRACT

The aqueous leaching of heavy metals from soft coal has been examined under a variety of conditions. Variables examined were pH, particle size, rate of flow, time of contact, and oxygen or nitrogen atmosphere. Simple leaching of coal from Western mines with pure water does not remove large amounts of metal. Metal removed was in most cases about 0.1% to 0.5% of the total metal in the coal. Extended, successive leaches (of about one week duration) and leaches in a mildly acid (acetic acid-acetate buffer; pH 4.7) tended to remove larger amounts of some metals. Leaching with a strong complexing agent removes relatively larger amounts of metal. When placed in contact with water previously spiked with metal ions, the coal actually reduces the aqueous concentration of many metal ions.

Continuous flow and simple shaker experiments correlate qualitatively with each other.

Considerable variation was found between Eastern and Western coal and also between different samples of Western coal.

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STATIC COAL STORAGE--CHEMICAL EFFECTS ON THE AQUATIC ENVIRONMENT

by

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FOREWORD

Attempts to predict the environmental impacts of greatly increased utilization of western coal clarified the need for data on the effects of each segment of the total coal-based fuel cycle, from the mine through transport, storage and conversion to electrical energy. In order to partially meet the need, a study was made of the environmental effects of the storage of western coal in large open-air holding piles in a transshipment facility located in the Superior, Wisconsin - Duluth, Minnesota harbor area.

This report presents the results of studies of the amounts of metals leached from a western and an eastern coal and the effects of these metals on several aquatic plant and invertebrate organisms.

Norbert A. Jaworski, Ph.D.
Director
Environmental Research Laboratory-Duluth

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ABSTRACT

The aqueous leaching of heavy metals from soft coal has been examined under a variety of conditions. Variables examined were pH, particle size, rate of flow, time of contact and oxygen or nitrogen atmosphere. Simple leaching of coal from Western mines with pure water does not remove large amounts of metal. Metal removed was in most cases about 0.1% to 0.5% of the total metal in the coal. Extended, successive leaches (of about one week duration) and leaches in a mildly acid (acetic acid-acetate buffer; pH≈4.7) tended to remove larger amounts of some metals. Leaching with a strong complexing agent removes relatively larger amounts of metal. When placed in contact with water previously spiked with metal ions, the coal actually reduces the aqueous concentration of many metal ions.

Continuous flow and simple shaker experiments correlate qualitatively with each other.

Considerable variation was found between Eastern and Western coal and also between different samples of Western coal.

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	-	Joseph Horton, Ph.D.
Staff	-	William Cook
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SECTION 1

GENERAL INTRODUCTION

The use of low-sulfur western coal, as an acceptable energy source has been on the increase for several years. A transshipment facility, located at Superior, Wisconsin has been established to service coal shipped from western mines. The coal is transported by rail to Superior, transferred to an open air holding pile, and then from the holding pile to freighters (modified iron ore carriers) which carry the coal by water to its final destination where it is used as fuel for a steam-driven electrical power plant. Approximately three quarter of a million tons of coal per year pass through the transshipment facility.

A chemical study was undertaken to determine the levels of EPA sensitive metals in the western coals, and to investigate the factors which determine the mobilization of the metals from the coal matrix. Determination of these parameters would give an index as to the probable effects of the transshipment of millions of tons of coal upon the water quality and upon the aquatic flora and fauna of the immediate area.

The chemistry study was performed to develop a reliable system and methodology for the determination of the leaching properties of coals, with respect to the mobilization and release of the environmentally sensitive metal content.

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SECTION 2

BROAD GENERAL CONCLUSIONS

1. Simple, slow percolation of relatively pure water (rain water or regular city water) does not leach heavy metals from western coal to any considerable extent. About 0.1 to 0.5% of trace metal content is so leached.

2. Heavy metal leaching would be enhanced by:

   a. very acid leachant: The coal is naturally self-buffered, and leachant in contact with the coal approaches a pH of greater than 7 pH units (slightly alkaline). Additional acid, of the order of magnitude of approximately 4 liters of concentrated sulfuric acid per ton of coal would be needed to overcome the self-buffering capacity of the system and allow the mobilization of dangerous amounts of heavy metal ions. Of the metals studied, leaching of barium and manganese are most enhanced by high acid levels.

   b. strong complexing agents: Complexing agents such as EDTA (ethylenediaminetetraacetic acid) are capable of removing relatively large amounts of heavy metals from the coal. This implies that leach waters, heavily loaded with organic materials, might extract more heavy metals than pure water.

   c. successive releaching with pure water: The leaching of heavy metals from coal appears to be an equilibrium process. Continuous application of fresh, relatively metal-free water, will eventually remove rather large amounts of heavy metal from the coal. This is not postulated here as any real environmental hazard. Assuming that long term releaching could remove about 5×10^{-6} g of manganese from 1 gram of western coal (based on the EDTA extraction work), a disaster which deposited about 50,000 metric tons of coal into the lake could contribute only about 0.3 ppb of Mn to 1 cubic kilometer of water. During EDTA extraction of western coals, manganese was extracted to the greatest extent. Other metals should give smaller effects.

3. There is excellent qualitative agreement between the results obtained from simple shaker extractions and those obtained from the more complex (and time consuming) continuous flow extractions. This would appear to be one of the most valuable results of this work as it establishes a reasonably firm basis for using shaker studies to survey the leaching properties of a variety of coal samples.

4. Western coal actually is an excellent sequesterer of metal ions at its naturally buffered pH of about 7.3. The spiked system uptake study shows

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that when the system is spiked with large concentrations of metal ions, the coal absorbs much more metal ion than it would release in equilibrium with distilled water. This suggests that if eastern (high sulfur) coal and western coal were to be used conjointly, storage of the western coal "downstream" from the eastern coal might be beneficial environmentally.

5. There appears to be significant differences in the leaching properties of different samples of western coal. This observation is in agreement with the work of Chadwick et al.[6] who did trace analyses on cores taken from a typical western coal seam. This implies that future leaching work should probably be based on a rather extensive and statistically significant sampling scheme.

6. Some attempts were made to formulate and fit an equilibrium mathematical model to the leaching system experimental data. Although some of the data showed promise in an approximate fit to a mathematical model, an overall match of a model to the total system was not clearly definitive, and thus was not reported. While the experimental data allowed certain qualitative conclusions to be drawn, the fluctuations in the limited pool of data were too broad to allow construction of a model which would show good agreement with experimental results.

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SECTION 3

RECOMMENDATIONS

The most obvious extension of this work would appear to be the development of a coal field survey technique. This would involve; (1) field geological sampling from the coal field, (2) trace metal leaching tests in the laboratory and (3) analysis of other coal parameters of interest.

The "on site" sampling would be a major project in itself. It would require a trained field geologist who would obtain proper "in situ" samples from the coal field. It is assumed that samples would be taken from selected test holes along the entire coal seam.

The laboratory leaching studies would involve deionized water leaching and EDTA (ethylenediaminetetraacetic acid) leaching of the samples. Shaker tests using 200 grams of ground and sieved coal for each liter of leachant would be used. Samples would be analyzed using flameless atomic absorption with a roulette type automatic sample feeder. The atomic absorption output could be interfaced with a digital computer for ease in data reduction.

The laboratory leaching work should be standardized as much as possible so that the method would give reliable comparisons between different coal seams.

The problem of filter absorption of trace metals during sample preparation has not been solved. Research on this problem should definitely be continued.

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SECTION 4

EXPERIMENTAL DESIGN AND PROCEDURES

GENERAL CONSIDERATIONS

The removal of heavy metals from coal by various aqueous leaching systems was investigated by both: A recirculating, continuous flow system and a shaker bath system. In these systems, various size fractions of ground coal samples were leached with several aqueous buffers. The leachants were analyzed for heavy metal content and the results were used to determine the degree of release of the metals from the coal particles.

6-1/2"

Western Coal No. 1

This coal was selectively sampled from one of the cars of a unit train which was transporting coal from the western mines to the Ortran transshipment facility in Superior, Wisconsin. The coal was collected and stored in polyethylene bags.

Western Coal No. 2

This sample was obtained from the Ortran storage pile at the Superior, Wisconsin transshipment facility. A bulldozer was used to remove the surface coal to a depth of about two meters. The coal sample was taken from the fresh surface exposed and stored in polyethylene bags.

Eastern Coal

This sample of coal from the eastern mines was furnished by the Detroit Edison Company. The sample was taken from a stockpile at the Detroit power plant and shipped to Superior in a polyethylene lined drum.

PREPARATION OF COAL SAMPLES

The original coal samples were:

(1) Air dried for approximately 24 hours to remove surface moisure.

(2) Ground with a single pass through a Thomas-Wiley® Laboratory Mill (Model 4) using a 2 mm exit screen.

(3) Successively halved by riffling through a stainless steel riffler to obtain small, uniform fractions of the original sample. All solder joints in the riffler were epoxy coated.

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(4) Sieved in a stainless steel sieve stack consisting of 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm and 0.63 mm sieves using a 15 minute shake on a Ro-Tap® shaker. The solder-free, stainless steel sieves were especially fabricated by the S. W. Tyler Company.

The sieved fractions were stored in closed, polypropylene containers until used.

MATERIALS AND REAGENTS

Deionized water was provided by a Millipore® system consisting of (1) a Milli-Q3® unit (prefiltration and reverse osmosis) followed by (2) a Milli-Q2® system of activated carbon and ion exchange resin cartridges. This deionized water gave zero blanks for all metals of interest when analyzed with the flameless atomic absorption spectrophotometer.

Other reagents were either analytical reagent or ultra-pure grade as required to give zero analytical blanks.

METAL ANALYSIS

The leachates were analyzed for metal content with a Perkin-Elmer®, Model 306, flameless atomic absorption spectrophotometer. Standard procedures were used [1,2,10,15]. Regular graphite tubes were used for earlier work. Pyrolyticgraphite-coated tubes [16] were introduced about half way through the project and used for the rest of the research.

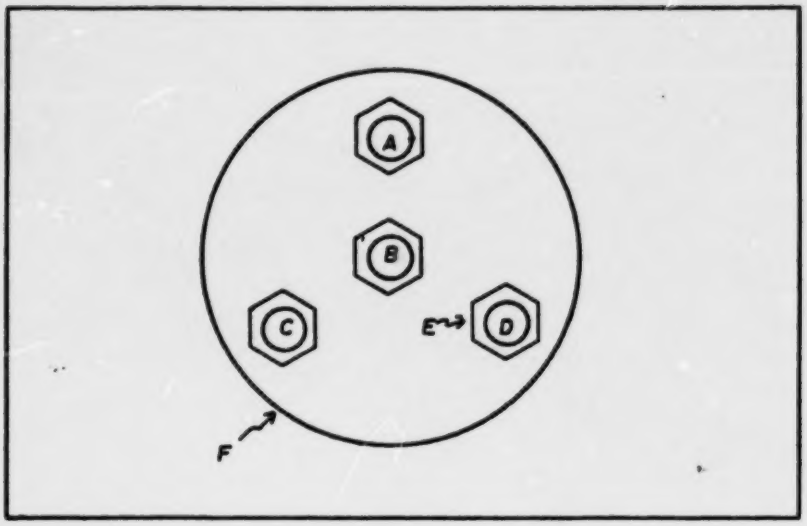
CONTINUOUS FLOW LEACHING APPARATUS

This apparatus was used in the studies which involved continuous flow of the leachant through the coal. See Figures 1, 2 and 3 for details of construction.

The interior contact surfaces of this apparatus consisted entirely of polypropylene, polytetrafluoroethylene (Teflon®) and flexible-silicone.

Six leaching bottles (see Figures 1 and 2) were mounted in a 300 liter, thermostated water bath. Flow patterns of gas and leachant are shown in Figure 3. The leachant was circulated by a six-head, single drive, variable speed, Master-flex® (Cole-Parmer), tubing pump system. Flexible-silicone was used for the pump tubing.

Each leaching bottle was a nominal 2-liter (one-half gallon) polypropylene bottle with a polypropylene screw cap. The various inlet and outlet tubes (see Figure 1) were fitted through the cap with polypropylene bulkhead fittings. The leachate outlet tube (see Figure 2) was fitted with a polypropylene thistle-tube top. The thistle-tube top was covered with a 74-micron Teflon® screen which was tied in place with a polypropylene fiber.



LEGEND FOR FIGURES 1 AND 2

A. LEACHATE INLET TUBE
B. LEACHATE OUTLET TUBE
C. GAS INLET TUBE
D. GAS OUTLET AND LIQUID VOLUME MAKEUP TUBE
E. BULKHEAD FITTING
F. BOTTLE CAP
G. 2-LITER LEACHING BOTTLE
H. THISTLE TUBE END
I. 74-MICRON TEFLON SCREEN

NOTE: ALL PARTS OF SYSTEM ARE POLYOLEFIN PLASTIC OR TEFLON.

Figure 1. Bottle Cap Schematic

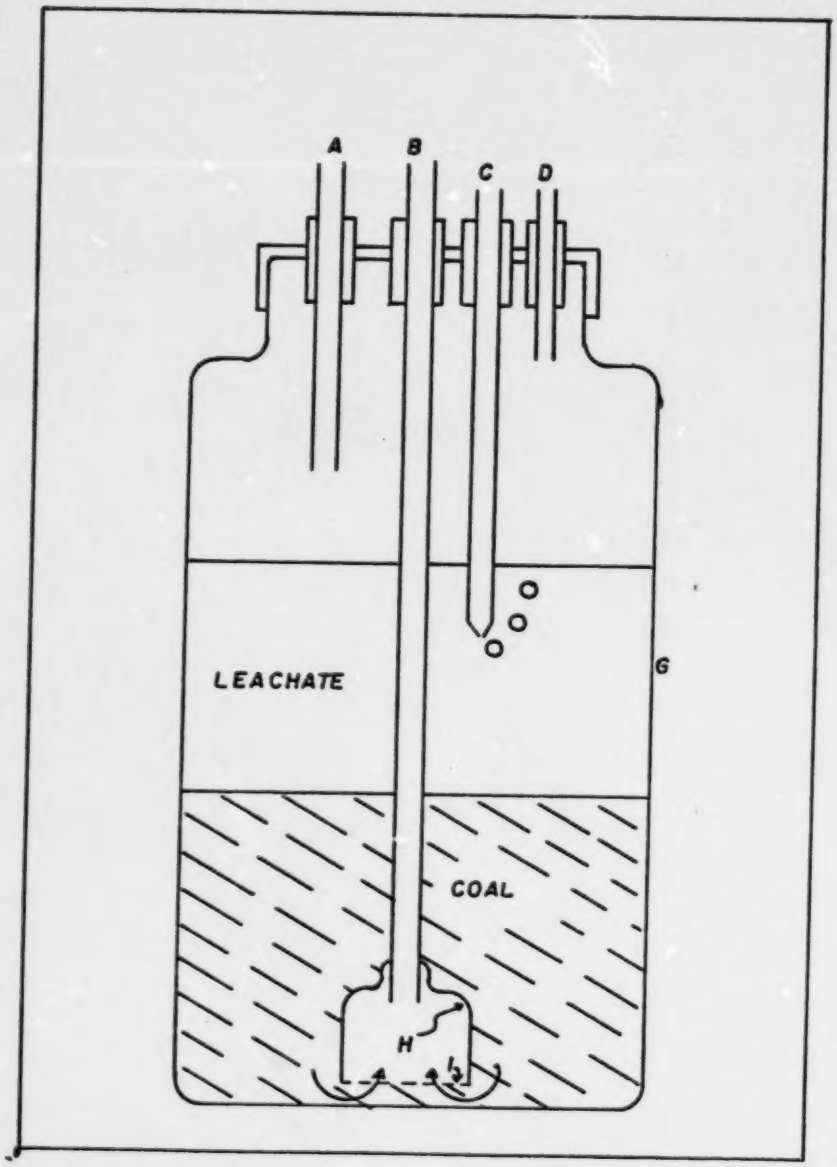


Figure 2. Leaching Bottle

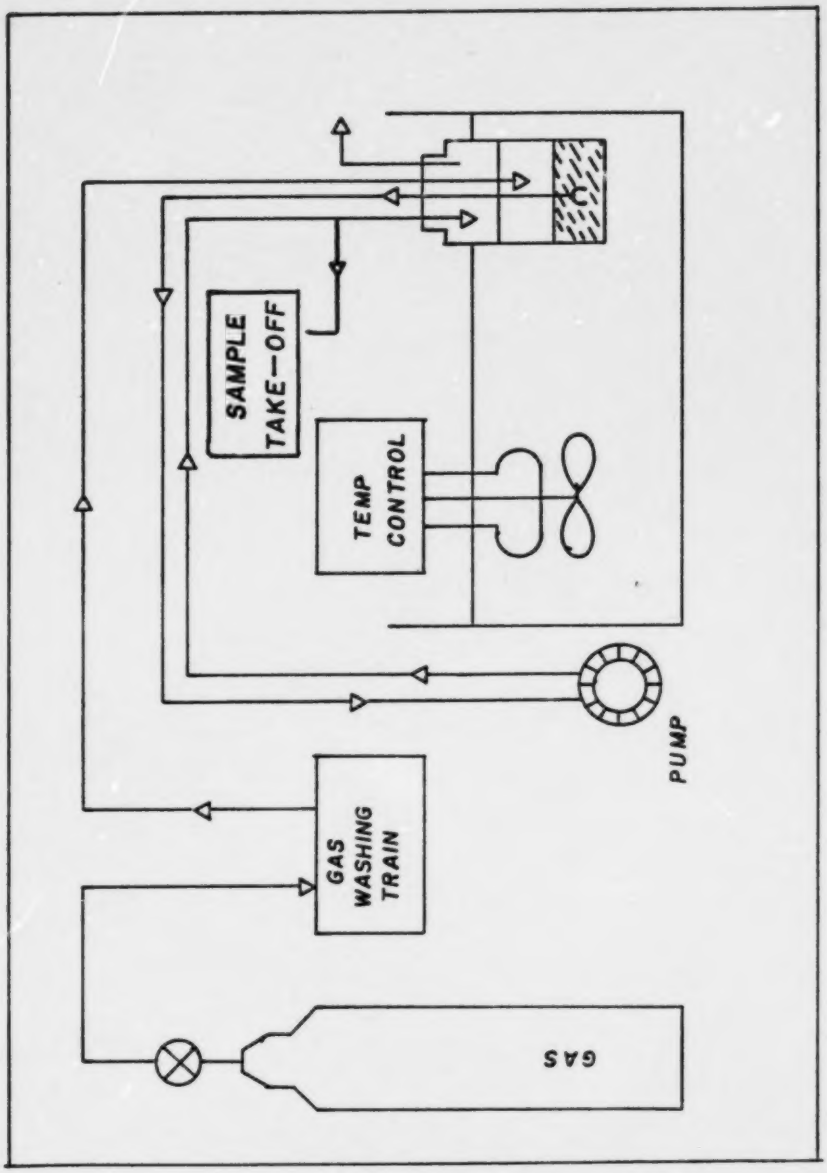


Figure 3. Continuous Flow Leaching System

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A dust protected tube was connected to the system through a valve and T- joint. This tube served as a sample withdrawal point (see Figure 3).

Commercial cylinder gases (nitrogen or oxygen) were purified by being passed through a surge tank and a seven-bottle washing train. The gases passed serially from the tanks through (1) a ballast bottle, (2) 6 N sulfuric acid, (3) 6 N sulfuric acid, (4) deionized water, (5) 6 N sodium hydroxide, (6) deionized water, and (7) deionized water. The surge tank and the ballast bottle were glass, the rest of the system was polypropylene and flexible-silicone. The gas washing train was pressurized to approximately 10 psig to ensure adequate control and passed through a splitting manifold to the leaching bottles.

SHAKER LEACHING PROCEDURES

Some of the leaching experiments were performed in a thermostated shaker bath. Charges of coal and leachant were placed in bottles (Teflon® or polypropylene), and secured to the sample tray of a Eberbach®, Model 6250 shaker bath. The shaking rate was adjusted to 45 cycles per minute. The shaker sample tray travel was adjusted to 28 mm.

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SECTION 5

EXPLORATORY EXPERIMENTS

COAL TITRATION

This experiment was formulated to give an approximate "equivalent weight" of the coal in terms of its ability to react with either acid or base.

Separate 2.00 gram samples of coal (Western Coal No. 1) were placed in prerinsed polyolefin bottles and covered with forty millimeters of deionized water. Particle sizes of coal used in the separate samples were:

1. 0.500 - 1.00 mm
2. 0.250 - 0.500 mm
3. 0.125 - 0.250 mm
4. 0.063 - 0.125 mm

Successive five ml portions of standard acid or base were added to each sample every 24 hours. The sample was then agitated and allowed to stand for a period of 24 hours, after which time, the pH of the system was measured with a pH meter.

Results and Discussion

A plot of pH versus ml of acid or base is shown in Fig. 4. The curve appears as a typical, multi-functional, weak acid or weak base titration curve. There is some effect due to particle size, with larger particle sizes showing a smaller buffer effect at higher pH values.

The buffer effect appears to be more of a bulk effect rather than a surface effect. With 35 ml of base added, the pH was about 9.5 for the largest particles and about 8.5 for the smallest particles. If there was no coal present, the pH should have been 11.7. A calculation showed that the 2.00 g of coal reacted with 2.1×10^{-3} mmoles of OH^- ion for the large particles and 4.2×10^{-3} mmoles of OH^- ion for the small particles. This is a 2 to 1 ratio. Assuming spherical particles and constant density, the small particles possess 8 times the surface area of the large particles. This observation indicates that the reaction of the coal with acid or base is primarily a bulk effect (depends more on mass than on surface area).

A calculation, using the data from this experiment, gives a value of 0.170 mmole H^+ required to bring 1 gram of coal suspension to pH = 4.85.

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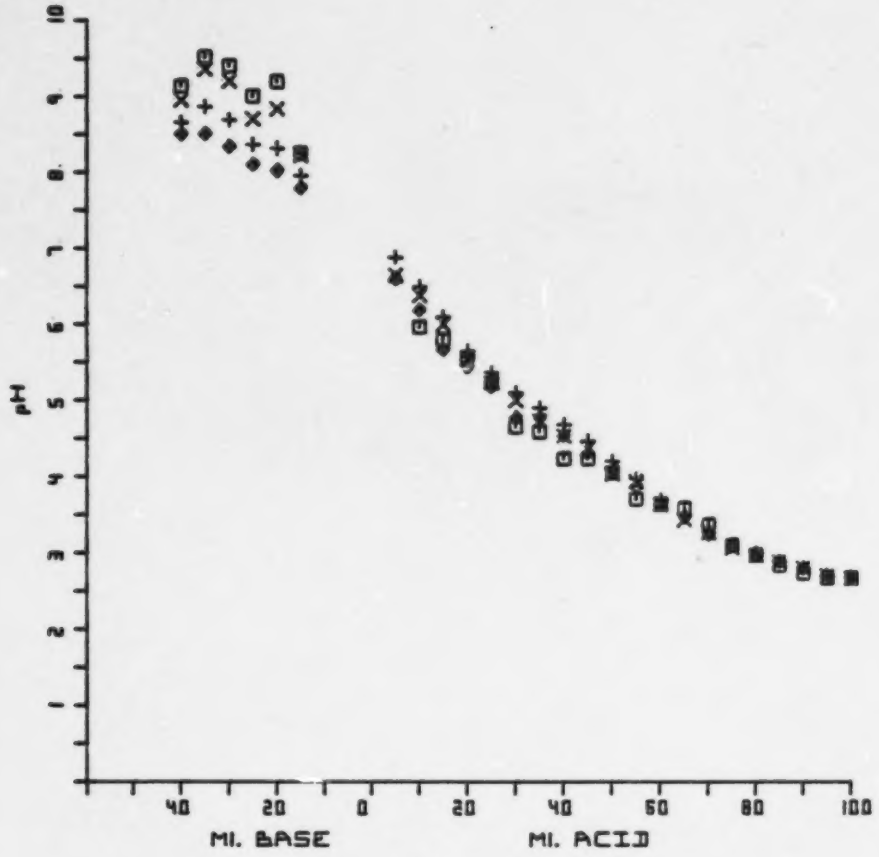

WESTERN COAL NO. 1
SAMPLE SIZE = 2.00 g.
HCl = 0.0106 N
NaOH = 0.0096 N
□ = 0.50 - 1.00 mm PARTICLE SIZE
× = 0.25 - 0.50 mm PARTICLE SIZE
\+ = 0.125 - 0.25 mm PARTICLE SIZE
◆ = 0.063 - 0.125 mm PARTICLE SIZE

Figure 4. Coal Titration

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DESIGN OF BUFFER SYSTEM FOR LOW pH RUNS

Western Coal produced slightly alkaline solutions in distilled water. In order to make leaching runs at pH values other than the natural buffer point of the coal, it became necessary to design buffer solutions.

Attempts were made to design:

1. an alkaline buffer near pH = 10 using Co_3^{2-}, HCO_3^- system
2. an acid buffer near pH = 5 and pH = 6 using a HCO_3-, H_2CO_3 system
3. an acid buffer near pH = 5 using a $C_2H_3O_2^-$, $HC_2H_3O_2$ system

Of the three systems, only system 3 was usable. The basic (near pH = 10) system gave leachates which were very concentrated in interferring materials (probably organic). These leachates actually blackened the quartz windows of the atomic absorption furnace and were thus impossible to analyze using the methods adopted for this work. The HCO_3^-, H_2CO_3 system would not hold pH due to escape of CO_2 to the atmosphere.

The final buffer of choice was 0.072 M $HC_2H_3O_2$ and 0.028 M Na $C_2H_3O_2$ in deionized water. Runs with this leachant are designated as "acetate buffer" runs. This system:

1. gave no background heavy metal contamination
2. gave no significant interferences in the atomic absorption analyses
3. held the pH of the system at 4.86 plus or minus a few tenths of pH unit during the leaching runs.

In the first set of leaching runs: 9 blank runs using the acetate buffer only, gave a final average $[H^+]$ of 5.36×10^{-5} with $\sigma = 0.64 \times 10^{-5}$. 18 runs with both buffer and coal gave a final average $[H^+]$ of 1.39×10^{-5} with $\sigma = 0.12 \times 10^{-5}$. These runs consisted of 1,000 ml of buffer solution and 200g of coal. Routine calculations with this data show that 0.16 mmoles of H^+ were neutralized by each gram of coal.

In comparison, the H Cl titration of the same coal gave 0.17 mmoles of H^+ neutralized by 1 gram of coal to reach an equivalent pH level.

FILTER UPTAKE STUDY

It was suspected that lead ion was adsorbed on Millipore® filters and thus lost to the analysis. A series of experiments were conducted to investigate this.

Samples of both deionized water and Lake Superior water were spiked with various concentrations of lead ion and the losses on filtering through 0.45 μ Millipore® filters were measured with the atomic absorption spectrophotometer. For the deionized water samples, filtration times were ∿3 min. Filtration times for the lake water runs were ∿2 min. Results are shown in

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Figures 5 and 6. One set of the filters from the deionized water runs were washed with 0.01 N HCl (ultra-pure) and another set of the filters were washed with a 1.0 ppm Al^{3+} ion solution (lead free). Lead was measured in these washings and these values were combined with the concentrations in the original filtrates to give total lead recovery with wash (see Fig. 7). These results imply that, at least at the higher concentrations of lead ion, significant amounts of lead are retained on the filters. Even though an acid or Lewis acid wash can recover this lead, the nature of the coal leaching system may not allow an acid wash or pretreatment of the sample before filtration.

At the 10 ppb level there was considerably less loss of lead from the lake water sample than from the deionized water sample. This protection of the lead ion, possibly by complexation, should be considerably enhanced in media such as coal leachates. Nevertheless this filter adsorption is of serious concern in any lead analysis of filtered water samples.

During all subsequent experiments, a metal was considered to be dissolved in the leachant if it passed through a 0.45μ filter. Any acid treatment of the leachate prior to filtration or acid wash of the filter would have disturbed the system by changing the properties of residual colloids and other particles in the system.

In this work, no lead was observed to leach from the coal with pure water.

A detailed study of filter absorption of metals from coal leachate would certainly be in order.

EXTREMUM RUNS

Preliminary to the large experimental designs, some coal was subjected to the extreme conditions that might be expected in the coal handling facility.

Experimental

Three samples of coal grindings were subjected to extreme conditions:

(1) One sample (50% coal - 50% water by weight) was shaken on a fast shaker at room temperature for 72 hours. The mud obtained was unfilterable. No analysis was done.

(2) One sample (50% coal - 50% water) was subjected to alternate freezing and thawing for 1 week under still (not shaken) conditions. Analytical results were Cu-4.0 ppb; Mn-2.1 ppb; Ba-70 ppb. V and Mo were below detection limits.

(3) One sample (50% coal - 50% water) was held near 100°C in a steam bath for 6 days. Analytical results were Cu-10.7 ppb; Mn-6.8 ppb; Ba-160 ppb. V and Mo were below detection limits.

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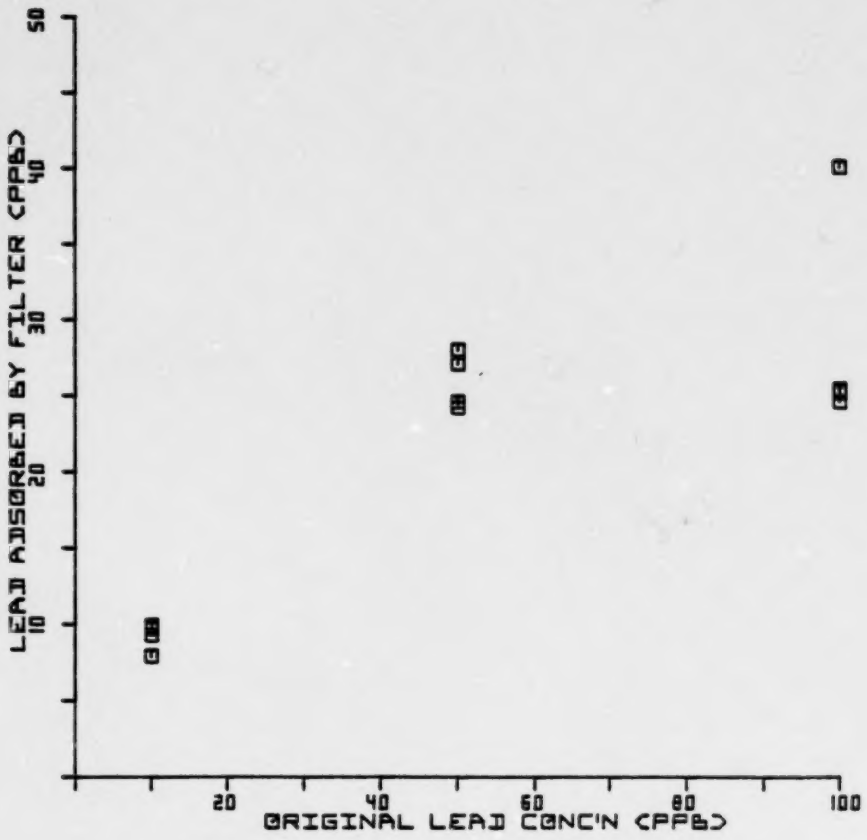


Figure 5. Filter Retention Study

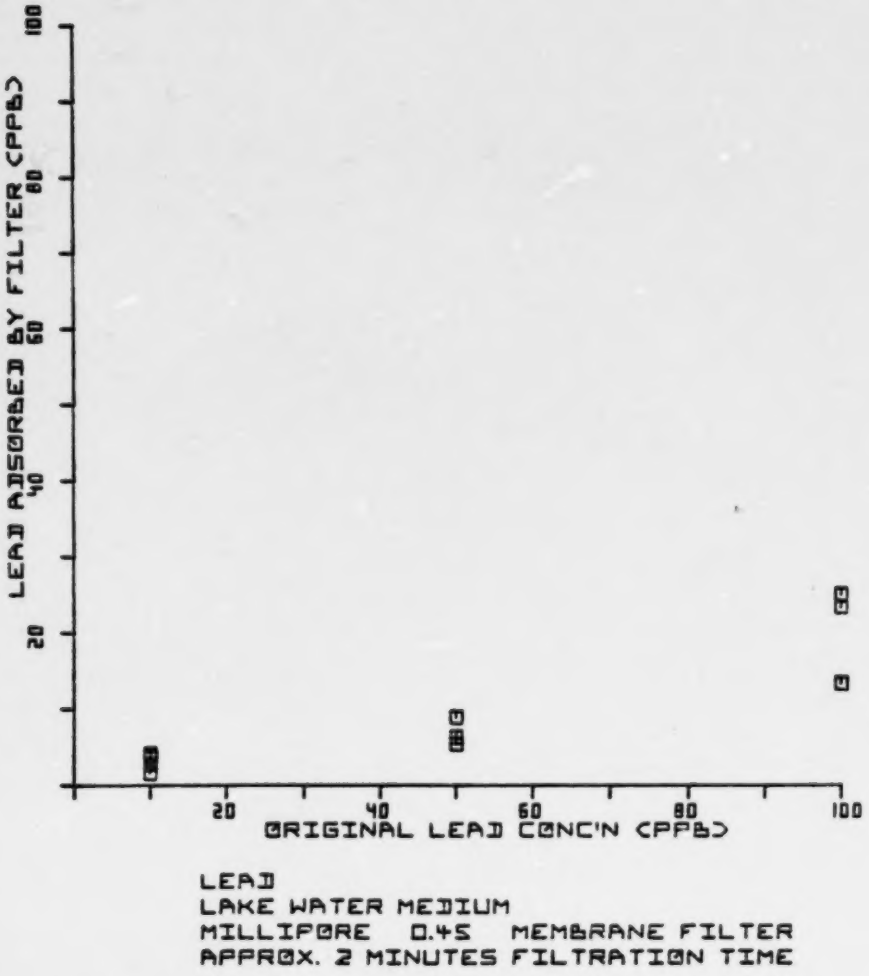
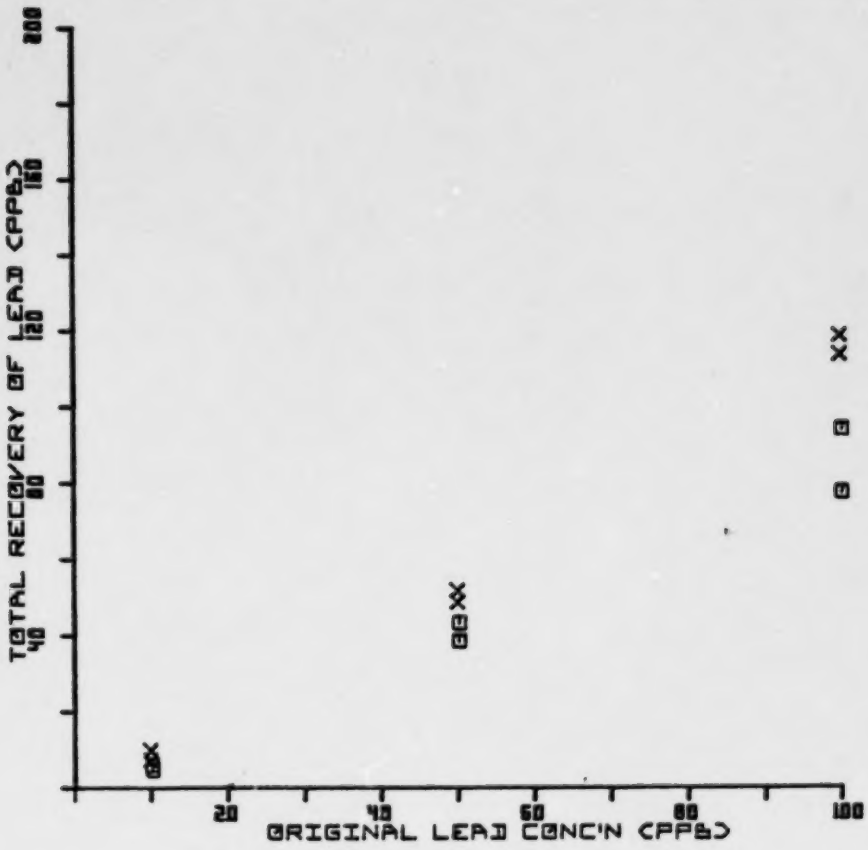


Figure 6. Filter Retention Study



LEAD
DEIONIZED WATER MEDIUM
MILLIPORE ® 0.45 μ MEMBRANE FILTER
APPROX. 3 MINUTE FILTRATION TIME
O : 0.1 M ALUMINUM ION WASH
X : 0.1 M HYDROCHLORIC ACID WASH

Figure 7. Filter Retention Study

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Discussion

Experiment (1) shows that the coal is rather fragile. As no analysis was done, no further conclusions were drawn.

Experiments (2) and (3) show a 2 to 3 fold increase in metal extraction for sub-boiling conditions over the extractions obtained for freeze-thaw conditions. Alternate freezing and thawing did not release large amounts of metal ions. Because many open storage piles will be subjected to moist, freeze-thaw cycles, this fact is certainly of environmental significance.

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SECTION 6

MAJOR METAL LEACHING EXPERIMENTS

FIRST FACTORIAL RUNS

Procedure

The first factorial runs were designed as an initial survey of the behavior of the continuous flow apparatus and the gross effects on heavy metal leaching of the variables studied.

The experiment consisted of a complete, single replicate factorial design on five variables at two levels each. Each run was sampled at 3 different times. This produced a pure 2^5 factorial design, overlain with a time parameter to give a pseudo $2^5 \times 3$ factorial experiment (32 separate runs). The variables and levels are listed in Table 1.

TABLE 1. VARIABLES FOR FIRST FACTORIAL RUNS

VARIABLE	SYMBOL	LEVEL 1	LEVEL 2
Temperature	T	20°C	40°C
Gas Saturation	G	N_2	O_2
Flow Rate	R	20 ml/min	80 ml/min
Particle Size	S	0.125 to 0.250 mm	0.500 to 1.00 mm
pH of leachate	P	Deionized water (pH reached ~ 7.3 in final leachate)	Acetate buffer (pH reached ~ 4.86 in final leachate)
Time	H	6 hours, 24 hours and 48 hours	

The "Western No 1" coal sample was used for this work. The atomic absorption analyses were done with unpyrolyzed graphite tubes.

The $T_2G_2R_1$ set of runs showed completely wild results. Gross contamination was suspected. The entire $T_2G_2R_1$ set was repeated and the repeat results used. The $T_2G_1R_1$ set of runs showed very wild results for Cu analysis. This set was repeated and the second set used for Cu analysis. This arbitrary repetition of selected runs in the factorial design was felt to be

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TABLE 2

FIRST FACTORIAL ANALYSIS - ARSENIC

Factor Code	Total Release Arsenic		
	6 Hr	24 Hr	48 Hr
$T_1G_1R_1S_1P_1$	1.20	0.56	0.88
$T_2G_1R_1S_1P_1$	2.80	2.44	2.35
$T_1G_2R_1S_1P_1$	1.50	0.87	1.11
$T_2G_2R_1S_1P_1$*	2.30	0.91	1.45
$T_1G_1R_2S_1P_1$	1.00	0.55	0.57
$T_2G_1R_2S_1P_1$	2.00	1.10	1.15
$T_1G_2R_2S_1P_1$	0.80	0.74	0.37
$T_2G_2R_2S_1P_1$	1.30	1.06	1.31
$T_1G_1R_1S_2P_1$	1.10	1.85	0.64
$T_2G_1R_1S_2P_1$	1.50	2.17	1.38
$T_1G_2R_1S_2P_1$	1.00	1.05	0.50
$T_2G_2R_1S_2P_1$*	1.50	1.37	1.24
$T_1G_1R_2S_2P_1$	0.80	0.64	0.67
$T_2G_1R_2S_2P_1$	1.10	0.75	0.69
$T_1G_2R_2S_2P_1$	0.40	1.02	0.67
$T_2G_2R_2S_2P_1$	2.00	2.50	1.02
$T_1G_1R_1S_1P_2$	1.50	1.87	1.76
$T_2G_1R_1S_1P_2$	2.30	2.51	4.13
$T_1G_2R_1S_1P_2$	2.60	2.13	3.33
$T_2G_2R_1S_1P_2$*	2.90	3.04	4.49
$T_1G_1R_2S_1P_2$	2.20	3.11	2.26
$T_2G_1R_2S_1P_2$	3.60	3.38	4.04
$T_1G_2R_2S_1P_2$	2.00	2.20	3.20
$T_2G_2R_2S_1P_2$	2.00	2.80	2.33
$T_1G_1R_1S_2P_2$	1.10	1.55	2.53
$T_2G_1R_1S_2P_2$	2.10	3.60	6.08
$T_1G_2R_1S_2P_2$	1.80	2.19	2.89
$T_2G_2R_1S_2P_2$*	2.30	3.01	4.06
$T_1G_1R_2S_2P_2$	1.70	2.38	3.40
$T_2G_1R_2S_2P_2$	2.90	3.34	4.10
$T_1G_2R_2S_2P_2$	1.80	1.89	2.88
$T_2G_2R_2S_2P_2$	2.00	2.50	4.52

*Values from replicate run were used.

TABLE 3

FIRST FACTORIAL ANALYSIS - BARIUM

Factor Code		Total Release Barium 6 Hr	24 Hr	48 Hr
$T_1G_1R_1S_1P_1$	High pH	45	27	29
$T_2G_1R_1S_1P_1$		90	60	67
$T_1G_2R_1S_1P_1$		65	48	36
$T_2G_2R_1S_1P_1$*		30	32	33
$T_1G_1R_2S_1P_1$		15	16	17
$T_2G_1R_2S_1P_1$		25	26	28
$T_1G_2R_2S_1P_1$		15	6	11
$T_2G_2R_2S_1P_1$		40	27	28
$T_1G_1R_1S_2P_1$		25	11	12
$T_2G_1R_1S_2P_1$		45	17	8
$T_1G_2R_1S_2P_1$		70	24	25
$T_2G_2R_1S_2P_1$*		26	10	11
$T_1G_1R_2S_2P_1$		30	17	7
$T_2G_1R_2S_2P_1$		25	21	12
$T_1G_2R_2S_2P_1$		5	10	6
$T_2G_2R_2S_2P_1$		10	11	11
$T_1G_1R_1S_1P_2$	Low pH	1470	1125	1035
$T_2G_1R_1S_1P_2$		2150	1810	1660
$T_1G_2R_1S_1P_2$		1570	1290	1100
$T_2G_2R_1S_1P_2$*		1650	1560	1675
$T_1G_1R_2S_1P_2$		1170	1150	895
$T_2G_1R_2S_1P_2$		1710	1325	1440
$T_1G_2R_2S_1P_2$		1300	1155	860
$T_2G_2R_2S_1P_2$		1770	1660	1350
$T_1G_1R_1S_2P_2$		1520	1365	1520
$T_2G_1R_1S_2P_2$		2260	2495	2490
$T_1G_2R_1S_2P_2$		2070	2145	1815
$T_2G_2R_1S_2P_2$*		1700	1695	1775
$T_1G_1R_2S_2P_2$		1390	1290	1350
$T_2G_1R_2S_2P_2$		2240	2060	1970
$T_1G_2R_2S_2P_2$		1350	1420	1435
$T_2G_2R_2S_2P_2$		1570	1430	1605

*Values from replicate runs used.

TABLE 4

FIRST FACTORIAL ANALYSIS - CHROMIUM

Factor Code	Total Release Chromium		
	6 Hr	24 Hr	48 Hr
$T_1G_1R_1S_1P_1$	0.40	0.42	0.54
$T_2G_1R_1S_1P_1$	0.50	0.32	0.84
$T_1G_2R_1S_1P_1$	0.20	0.21	0.22
$T_2G_2R_1S_1P_1^*$	0.50	0.52	0.95
$T_1G_1R_2S_1P_1$	0.20	0.21	0.21
$T_2G_1R_2S_1P_1$	0.40	0.22	0.83
$T_1G_2R_2S_1P_1$	0.00	0.20	0.01
$T_2G_2R_2S_1P_1$	0.30	0.31	0.33
$T_1G_1R_1S_2P_1$	0.20	0.21	0.22
$T_2G_1R_1S_2P_1$	0.00	0.00	0.00
$T_1G_2R_1S_2P_1$	0.20	0.01	0.01
$T_2G_2R_1S_2P_1^*$	0.20	0.21	0.22
$T_1G_1R_2S_2P_1$	0.20	0.21	0.22
$T_2G_1R_2S_2P_1$	0.20	0.21	0.22
$T_1G_2R_2S_2P_1$	0.00	0.20	0.01
$T_2G_2R_2S_2P_1$	0.20	0.21	0.52
$T_1G_1R_1S_1P_2$	0.00	0.20	0.01
$T_2G_1R_1S_1P_2$	0.00	0.00	0.00
$T_1G_2R_1S_1P_2$	0.00	0.00	0.20
$T_2G_2R_1S_1P_2^*$	0.00	0.70	0.23
$T_1G_1R_2S_1P_2$	0.00	0.00	0.00
$T_2G_1R_2S_1P_2$	0.20	0.01	0.01
$T_1G_2R_2S_1P_2$	0.00	0.00	0.00
$T_2G_2R_2S_1P_2^*$	0.20	0.21	0.22
$T_1G_1R_1S_2P_2$	0.00	0.40	0.22
$T_2G_1R_1S_2P_2$	0.20	0.01	0.01
$T_1G_2R_1S_2P_2$	0.00	0.00	0.00
$T_2G_2R_1S_2P_2$	0.20	0.21	0.22
$T_1G_1R_2S_2P_2$	0.00	0.00	0.00
$T_2G_1R_2S_2P_2$	0.20	0.21	0.02
$T_1G_2R_2S_2P_2$	0.00	0.00	0.00
$T_2G_2R_2S_2P_2$	0.20	0.31	0.02

*Values from replicate runs used.

TABLE 5

FIRST FACTORIAL ANALYSIS - COPPER

	Total Release Copper		
Factor Code	6 Hr	24 Hr	48 Hr
$T_1G_1R_1S_1P_1$	2.7	3.0	2.1
$T_2G_1R_1S_1P^*_1$	1.1	3.8	2.2
$T_1G_2R_1S_1P_1$	1.3	1.4	0.7
$T_2G_2R_1S_1P^*_1$	2.8	2.1	2.4
$T_1G_1R_2S_1P_1$	7.7	2.7	2.3
$T_2G_1R_2S_1P_1$	1.9	2.5	2.1
$T_1G_2R_2S_1P_1$	3.2	1.7	2.1
$T_2G_2R_2S_1P_1$	2.2	1.4	1.2
$T_1G_1R_1S_2P_1$	3.2	1.3	1.7
$T_2G_1R_1S_2P^*_1$	1.8	1.7	2.5
$T_1G_2R_1S_2P_1$	4.2	2.5	1.6
$T_2G_2R_1S_2P^*_1$	1.3	1.7	1.4
$T_1G_1R_2S_2P_1$	1.3	1.1	1.1
$T_2G_1R_2S_2P_1$	3.5	3.5	1.7
$T_1G_2R_2S_2P_1$	1.5	1.6	1.2
$T_2G_2R_2S_2P_1$	1.7	1.4	4.2
$T_1G_1R_1S_1P_2$	2.1	2.5	3.2
$T_2G_1R_1S_1P^*_2$	2.0	3.2	6.7
$T_1G_2R_1S_1P_2$	3.5	2.8	1.4
$T_2G_2R_1S_1P^*_2$	1.8	2.1	3.2
$T_1G_1R_2S_1P_2$	1.3	1.6	1.6
$T_2G_1R_2S_1P_2$	1.9	1.6	2.1
$T_1G_2R_2S_1P_2$	1.8	1.9	1.1
$T_2G_2R_2S_1P_2$	12.9	2.1	2.7
$T_1G_1R_1S_2P_2$	1.8	2.4	3.5
$T_2G_1R_1S_2P^*_2$	1.1	2.1	0.9
$T_1G_2R_1S_2P_2$	2.0	1.8	2.2
$T_2G_2R_1S_2P^*_2$	3.2	2.2	2.8
$T_1G_1R_2S_2P_2$	1.6	1.2	1.9
$T_2G_1R_2S_2P_2$	1.3	1.8	2.5
$T_1G_2R_2S_2P_2$	2.5	1.4	1.4
$T_2G_2R_2S_2P_2$	10.8	3.0	3.5

*Values from replicate runs used.

TABLE 6

FIRST FACTORIAL ANALYSIS - MANGANESE

Factor Code		Total Release Manganese 6 Hr	24 Hr	48 Hr
$T_1G_1R_1S_1P_1$	High pH	0.8	0.9	1.1
$T_2G_1R_1S_1P_1$		1.4	1.5	2.4
$T_1G_2R_1S_1P_1$		0.8	0.7	0.7
$T_2G_2R_1S_1P_1$*		1.8	1.1	1.3
$T_1G_1R_2S_1P_1$		0.9	0.5	0.5
$T_2G_1R_2S_1P_1$		0.8	1.0	1.3
$T_1G_2R_2S_1P_1$		0.4	0.3	0.5
$T_2G_2R_2S_1P_1$		1.1	1.1	1.2
$T_1G_1R_1S_2P_1$*		0.5	0.4	0.4
$T_2G_1R_1S_2P_1$		0.7	0.4	0.6
$T_1G_2R_1S_2P_1$		0.7	0.3	0.5
$T_2G_2R_1S_2P_1$		0.5	0.8	0.7
$T_1G_1R_2S_2P_1$		0.5	0.3	0.4
$T_2G_1R_2S_2P_1$		0.5	0.5	0.6
$T_1G_2R_2S_2P_1$		0.2	0.2	0.2
$T_2G_2R_2S_2P_1$		0.5	0.5	0.9
$T_1G_1R_1S_1P_2$	Low pH	120	144	197
$T_2G_1R_1S_1P_2$		113	131	147
$T_1G_2R_1S_1P_2$		114	134	142
$T_2G_2R_1S_1P_2$*		105	129	140
$T_1G_1R_2S_1P_2$		111	124	135
$T_2G_1R_2S_1P_2$		117	127	158
$T_1G_2R_2S_1P_2$		118	139	146
$T_2G_2R_2S_1P_2$		105	139	154
$T_1G_1R_1S_2P_2$		114	126	145
$T_2G_1R_1S_2P_2$		91	116	138
$T_1G_2R_1S_2P_2$		96	121	133
$T_2G_2R_1S_2P_2$*		93	124	134
$T_1G_1R_2S_2P_2$		99	112	128
$T_2G_1R_2S_2P_2$		102	122	133
$T_1G_2R_2S_2P_2$		96	135	142
$T_2G_2R_2S_2P_2$		106	138	144

*Values from replicate runs used.

warranted based on the strong evidence of sample contamination.

Results

Analysis was started on 13 metals during the initial stage of this experiment, but was completed for the full factorial set of 96 samples on only 5 of these metals (As, Ba, Cr, Cu and Mn). The remaining 8 metals showed values at or below detection limits in the early analysis. In order to save time, these metals (Cd, Co, Pb, Mo, Ni, Se, V and Zn) were analyzed on a reduced factorial basis. That is, only those samples which had N_2 gas (G_1), particle size of 0.125 to 0.250 mm (P_1) and 24 hour sampling time (H_2) were analyzed. This gave a 2^3 factorial on temperature, flow rate and pH.

Total release data for the complete factorial analyses for As, Ba, Cr, Cu and Mn are given in Tables 2 through 6.

The original statistical analysis of these data were done using a 2^6 factorial method developed by Yates[7]. The data were later refined using the ANOVAR program from the "Dartmouth Statistical Package."[1] The ANOVAR program allowed a $2^5 \cdot 3^1$ analysis (time at 3 levels). The ANOVAR results are discussed below:

Arsenic--

Using 3rd, 4th and 5th order interactions as a pooled error estimate gives the following variables and interactions as significant:

Extremely Significant:	$\alpha << 0.001$	T, P, HP
Highly Significant:	$\alpha < 0.001$	GRP, H
Very Significant:	$\alpha < 0.01$	TG, SH, SHP
Significant:	$\alpha < 0.025$	RP, GRS

The significance of so many variables imply a fairly complex mechanism for leaching.

The combined effects T, P, H and HP account for 76.7% of the total sum of squares in the analysis.

The main effects T, P and H are outlined in Table 7.

TABLE 7. MAIN EFFECTS: ARSENIC

Effect	Absolute difference in amount of metal leached (between levels)	Difference expressed as % of the overall mean
$\bar{T}_2 - \bar{T}_1$	+0.847 ppb	+42.8
$\bar{P}_2 - \bar{P}_1$	+1.55 ppb	+78.3
$\bar{H}_3 - \bar{H}_1$	+0.466 ppb	+23.5

Barium--

It is immediately obvious from Table 3 that pH has a very large effect on barium leaching. The grand mean of the high pH runs is 26.4 ppb of Ba while the grand mean at low pH is 1,580 ppb. That is, an increase of approximately 60 fold is observed in Ba leaching when the system is buffered to high H^+ concentrations.

From a statistical viewpoint, these data must be treated as two separate experiments. Otherwise, the lack of a homogeneity of variance would vitiate any analysis of variance treatment. Therefore, the high and low pH runs were split and run on the ANOVAR program as two separate $2^4 \times 3^1$ designs.

The high pH (low H^+) runs: Using 3rd and 4th order interactions as a pooled error estimate gives the following variances and interactions as significant:

Highly Significant:	$\alpha<<0.001$	R, S
Very Significant:	$\alpha<0.01$	TGR, H, TG
Significant:	$\alpha<0.025$	RS, GRS

The main effects R, S and H are outlined in Table 8.

TABLE 8. MAIN EFFECTS: BARIUM AT HIGH pH

Effect	Absolute difference in amount of metal leached (between levels)	Difference expressed as % of the overall mean
$\bar{R}_2 - \bar{R}_1$	-17.79 ppb	-67.51
$\bar{S}_2 - \bar{S}_1$	-15.29 ppb	-58.03
$\bar{H}_3 - \bar{H}_1$	-13.75 ppb	-52.18

Thus it is seen that leaching is enhanced by slower flow rates, smaller particle size and shorter residence times. The apparent inverse effect of time is possibly due to some sort of redeposition process; either on the system walls or on the coal.

The R, S and H effects account for 44.2% of the total sum of squares.

The low pH (high H^+) runs: Using 3rd and 4th order interactions as a pooled error estimate gives the following variables and interactions as significant:

Extremely Significant:	$\alpha<<<0.001$	T, S
Highly Significant:	$\alpha<0.001$	R, TG, TGS
Very Significant:	$\alpha<0.01$	H
Significant:	$\alpha<0.025$	SH

The main effects T, S, R and H are outlined in Table 9.

TABLE 9. MAIN EFFECTS: BARIUM AT LOW pH

Effect	Absolute difference in amount of metal leached (between levels)	Difference expressed as % of the overall mean
$\bar{T}_2 - \bar{T}_1$	+427.4 ppb	+27.0
$\bar{S}_2 - \bar{S}_1$	+336.8 ppb	+21.3
$\bar{R}_2 - \bar{R}_1$	-252.0 ppb	-15.9
$\bar{H}_3 - \bar{H}_1$	-182.1 ppb	-11.5

The T, S, R and H effects account for 65.6% of the total sum of squares.

As in the high pH runs, slower rate of pumping and shorter residence times give greater leaching. Temperature, which was not a main effect in the high pH runs becomes the major variable at low pH. The strange effect of increased leaching with larger particle size is difficult to explain.

Chromium--

Using 3rd, 4th and 5th order interactions as a pooled error estimate gives the following variables and interactions as significant:

Extremely Significant:	$\alpha << 0.001$	T, P
Highly Significant:	$\alpha < 0.001$	S, TG, SP
Very Significant:	$\alpha < 0.01$	T, TGR, TS, RS, GSP, HP, THP
Significant:	$\alpha < 0.025$	RSP, GP

The main effects T, R, S and P are outlined in Table 10.

TABLE 10: MAIN EFFECTS: CHROMIUM

Effect	Absolute difference in amount of metal leached (between levels)	Difference expressed as % of the overall mean
$\bar{T}_2 - \bar{T}_1$	+0.1304 ppb	+72.2
$\bar{R}_2 - \bar{R}_1$	-0.0517 ppb	-28.6
$\bar{S}_2 - \bar{S}_1$	-0.0983 ppb	-54.4
$\bar{P}_2 - \bar{P}_1$	-0.1688 ppb	-93.4

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The leaching of chromium seems to be enhanced at higher temperatures, slower pumping rate, smaller particle size and lower hydrogen ion concentration (higher pH).

Even with the large number of significant interactions, the four main effects account for 36.6% of the total sum of squares.

The grand mean for total release of chromium in this experiment was 0.181 ppb. The detection limit for chromium (for unpyrolized tubes) is 0.52 ppb. This comparison obviously casts some doubt on the above results. Even so, the main effects are probably real and the large number of significant interactions indicates a complex leaching mechanism.

Copper--

The results for copper seem to vary on a random basis. The grand mean for the data is 2.41 ppb with an overall standard deviation of 1.75. This yields a Cu value at 95% confidence limits of 2.41 ± 0.36 ppb.

The ANOVAR analysis showed a vary confused picture. Using 3rd, 4th and 5th order interactions for an error estimate gives an $s_{(error)} = 1.42$ (almost as large as the overall s value). Two interactions: PG and GHP were the most significant at $\alpha < 0.025$. With 63 variables and interactions in the design, one would expect about 1.6 effects to show an α this small on a random basis. Therefore, the statistical analysis of the Cu data was terminated at this point.

Manganese--

As in the barium results, manganese leaching is very strongly affected by changes in pH. The grand mean for the high pH runs is 0.748 ppb while the grand mean for the low pH runs is 127 ppb. Therefore, the manganese results were split into two $2^4 \times 3^1$ factorial designs for analysis.

The high pH (low H^+) runs: Using 3rd and 4th order interactions as a pooled error estimate gives the following variables and interactions as significant:

Highly Significant:	$\alpha < 0.001$	T, S
Very Significant:	$\alpha < 0.01$	R, TS

The main effects T, S and R are outlined in Table 11.

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TABLE 11. MAIN EFFECTS: MANGANESE AT HIGH pH

Effect	Absolute difference in amount of metal leached (between levels)	Difference expressed as % of the overall mean
$\bar{T}_2 - \bar{T}_1$	+0.438 ppb	+48.6
$\bar{S}_2 - \bar{R}_1$	-0.513 ppb	-68.6
$\bar{R}_2 - \bar{R}_1$	-0.254 ppb	-34.0

T, S and R account for 68.3% of the total sum of squares.

At high pH, manganese leaching is enhanced by high temperatures, small particle size and slow pumping rate.

The low pH (high H^+) runs: Using 3rd and 4th order interactions as a pooled error estimate gives the following variables and interactions as significant:

Extremely Significant:	$\alpha << 0.001$	H
Highly Significant:	$\alpha < 0.001$	S
Very Significant:	$\alpha < 0.01$	GR, TR

The main effects H and S are given in Table 12.

TABLE 12. MAIN EFFECTS: MANGANESE AT LOW pH

Effect	Absolute difference in amount of metal leached (between levels)	Difference expressed as % of the overall mean
$\bar{H}_3 - \bar{H}_1$	+38.5 ppb	+30.4
$\bar{S}_2 - \bar{S}_1$	-12.5 ppb	-9.87

The main effects H and S account for 75.5% of the total sum of squares.

At low pH, manganese leaching is enhanced by long leaching times and small particle size.

Summary of Results

The major conclusions concerning the effects of the variables on metal leaching from the coal samples are:

(1) Most of the variables seem to be significant to some extent.

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(2) An acetate buffer solution has a striking effect on barium and manganese.

(3) The overall mechanism seems to be very complex with considerable variation from metal to metal.

Reduced Factorial Analyses

The results of the reduced factorial are given in Table 13. The concentrations of these metals over the conditions studied are near or below detection limits. The only obvious trends are (a) Selenium seems to extract better at high pH and (b) Molybdenum seems to extract better at low pH.

TABLE 13

RESULTS OF REDUCED FACTORIAL

Raw Data at 24 hr. Sample Time Metal Concentrations in ppb

	Cd	Co	Pb	Mo	Ni	Se	V	Zn
$T_1R_1P_1$	0.00	0.7	0.9	0.3	5.0	3.5	0.0	1.9
$T_2R_1P_1$	0.01	1.4	1.9	3.2	7.9	2.4	2.5	4.2
$T_1R_2P_1$	0.18	0.5	1.2	0.6	1.6	2.7	0.0	0.7
$T_2R_2P_1$	0.12	0.6	0.4	2.6	7.9	3.1	0.0	1.9
$T_1R_1P_2$	0.02	1.0	0.1	10.0	5.5	1.2	2.5	5.0
$T_2R_1P_2$	0.07	0.7	0.5	11.3	3.4	1.2	0.0	2.6
$T_1R_2P_2$	0.16	0.3	0.0	10.7	21.1	1.2	0.0	0.0
$T_2R_2P_2$	0.57	5.4	0.2	10.0	2.9	1.0	0.0	0.2
Detection Limit	0.08	1.0	0.47	6.6	4.1	---	2.4	0.18

CONTINUOUS FLOW RELEACHING RUNS

Experimental

The purpose of this study was to determine the quantity of metal iron which would be mobilized by sequential changes in fresh leachant.

The continuous flow releaching experiments were done in the set-up which was employed in the first factorial experiment and the releaching factorial experiment (see appropriate sections of this report).

Experimental conditions were held as listed in Table 14.

TABLE 14. EXPERIMENTAL CONDITIONS FOR CONTINUOUS FLOW RELEACHING

Variable	Set 1	Set 2
Coal	Western Coal No. 1	Same
Particle Size	0.250 - 0.500 mm	Same
Leachant	Deionized Water	Acetate Buffer
Flow Rate	20 ml/min	Same
Temperature	40°C	Same
Sampling Times	48, 96, 144, 192 hrs.	Same
Leachant Replacement	48, 96, 144 hrs.	Same
Atmosphere	Air	Same

Coal - Western Coal No. 1 was dried, ground and sieved as previously described. See Section V-b.

Leachant - Two different types of leachant were used in this experiment:
1. Deionized Water
2. Acetate Buffer (see section 5)

The different leachants were used to determine the difference in behavior of the coal at two levels of pH.

Procedure - Duplicate samples were prepared, containing 200 grams of Western Coal No. 1 (0.250 - 0.500 mm size) and 1000 ml of the two types of leachant. This allowed replicate runs to be performed with each leachant system, thus giving better analytical control for statistical purposes. Samples were withdrawn, leachant replaced and the stabilized leachates were analyzed by flameless atomic

absorption spectrophotometry.[1, 2, 11, 15, 16]

Samples were taken at 48, 96, 144 and 192 hrs (termination of the experiment). At each sampling, except the last, 800 ml of leachate was removed and replaced with an equivalent volume of fresh leachant of the appropriate type.

A portion of the fresh leachate was used for pH determination. Other portions of the leachate were filtered, with suction, through a 0.45 micron membrane filter and acidified with ultrapure nitric acid to stabilize them for storage and analysis.

Results and Discussion

Total release values versus time are listed in Tables 15 and 16.

The nickel samples were lost to analysis because of nickel contamination.

The main features of these results are: (1) metal continues to be removed from the coal with repeated leachings (except perhaps for selenium in the acetate buffer), (2) greater amounts of metal are leached by the low pH (acetate buffer) leachant (except for copper, selenium and zinc), (3) excellent agreement between the paired runs is obtained (except for chromium and manganese in deionized water and copper and selenium in the acetate buffer). Even the worst cases are not too far off considering the inherent errors of this type of system.

TABLE 15

CONTINUOUS FLOW RELEACHING RESULTS

DEIONIZED WATER LEACH

Coal/H_2O Ratio 0.2g/1.0g

	48 Hr.		96 Hr.		144 Hr.		192 Hr.	
	Total Release in ppb	Avg. in ppb	Total Release in ppb	Avg. in ppb	Total Release in ppb	Avg. in ppb	Total Release in ppb	Avg. in ppb
As	1.5 1.7	1.6	2.0 1.9	2.0	2.7 2.6	2.7	2.9 3.0	3.0
Ba	42.0 38.0	40.0	45.6 41.4	43.5	52.2 48.2	50.2	56.4 52.4	54.4
Cd	1.1 1.1	1.1	1.6 1.2	1.4	1.9 1.5	1.7	2.0 1.7	1.9
Cr	0.4 0.2	0.3	0.4 0.3	0.4	0.8 0.5	0.7	0.8 0.6	0.7
Co	0.1 0.1	0.1	0.4 0.4	0.4	0.6 0.6	0.6	0.8 0.8	0.8
Cu	4.7 4.0	4.4	4.8 5.1	5.0	6.8 6.9	6.9	8.5 7.7	8.1
Pb	0.4 0.0	0.2	0.3 0.0	0.2	0.3 0.0	0.2	0.3 0.0	0.2
Mn	2.2 1.3	1.8	2.3 1.4	1.9	2.5 1.8	2.2	2.8 2.1	2.3
Mo	0.7 1.0	0.9	1.7 1.8	1.8	2.4 2.7	2.6	2.8 2.8	2.8
Se	2.0 1.0	1.5	3.6 2.8	3.2	3.2 4.4	3.8	6.2 7.0	6.6
V	0.0 0.0	0.0	0.0 0.0	0.0	0.0 0.0	0.0	0.0 0.0	0.0
Zn	2.3 1.4	1.9	2.4 1.6	2.0	3.6 3.3	3.5	8.6 3.9	6.3

TABLE 16

CONTINUOUS FLOW RELEACHING RESULTS

ACETATE BUFFER SOLUTION LEACH

Coal/Buffer Ratio 0.2 /1.0

	48 Hr.		96 Hr.		144 Hr.		192 Hr.	
	Total Release in ppb	Avg. in ppb	Total Release in ppb	Avg. in ppb	Total Release in ppb	Avg. in ppb	Total Release in ppb	Avg. in ppb
As	6.6 6.7	6.7	13.6 13.3	13.5	19.8 20.4	20.1	25.3 24.9	25.1
Ba	970 890	930	2410 2610	2510	3760 3940	3850	5590 5910	5750
Cd	1.7 2.3	2.0	2.7 2.8	2.8	3.9 3.8	3.9	4.5 4.0	4.3
Cr	0.8 0.9	0.9	1.7 1.3	1.5	2.0 2.0	2.0	2.5 2.5	2.5
Co	1.5 1.4	1.5	2.6 2.9	2.8	4.0 4.2	4.1	4.9 4.9	4.9
Cu	4.1 1.8	3.0	4.8 2.5	3.7	5.0 2.7	3.9	5.4 4.1	4.8
Pb	0.0 0.0	0.0	0.0 0.0	0.0	0.0 0.0	0.0	0.0 0.0	0.0
Mn	181 154	168	295 271	283	425 395	410	543 510	527
Mo	14.0 13.5	13.8	22.6 22.3	22.5	29.6 31.4	30.5	32.1 33.3	32.7
Se	1.0 1.0	1.0	1.8 0.8	1.3	1.6 0.8	1.2	1.6 0.8	1.2
V	0.0 0.0	0.0	0.0 0.0	0.0	0.0 0.0	0.0	0.0 0.0	0.0
Zn	1.6 1.7	1.7	3.1 3.4	3.3	3.5 4.9	4.2	5.4 7.0	6.2

RELEACHING SHAKER RUNS

Experimental

The purpose of the releaching shaker runs was to determine how much additional metal could be removed from the coal by the use of additional passes of leachant and to compare the results with those from the continuous flow releaching runs.

Two 1000 ml Teflon® bottles were charged with 100 gram portions of 0.250-0.500 mm sized Western Coal No. 1. Deionized water (500 ml) was added to one bottle, and 500 ml of acetate buffer was added to the other coal sample.

The two bottles were placed in a heated shaker bath, which was maintained at 40°C for the duration of the run. Shaking rate was 45 cycles per minute, with a travel of 28 mm by the shaker sample tray. Samples were collected at 48, 96, 144, 192 and 288 hours respectively.

At the time of sampling, 400 ml of each leachant was removed and the same volume of the appropriate fresh leachant was added to the bottles. This volume represented an 80 percent replacement of leachant volume at each sampling time.

The pH of the leachates were determined at the time of sampling, and then filtered through a 0.45 micron membrane filter. The filtered samples were acidified with ultrapure nitric acid to stabilize them for storage, and the metals were determined by flameless atomic absorption spectrophotometry.[1, 2, 11, 15, 16] All metals except mercury were determined.

Results and Discussion

Total release values versus time are listed in Table 17.

The nickel samples were lost to analysis because of nickel contamination. The zinc values appeared to be very badly contaminated.

The salient features of these results are: (1) metal continues to be removed from the coal with repeated releachings (except perhaps for selenium), (2) greater amounts of metal are leached by the low pH (acetate buffer) leachant (except for chromium and selenium).

The generally strong agreement of these date with the data on releaching in the continuous flow system is extremely important. Shaker studies have long been used for coal leaching work, but there seemed to be some doubt that such quick and easy experiments would give results analogous to a continuous flow system. It would seem that this work would place shaker studies on a more firm foundation.

A comparison of the continuous flow and shaker releaching runs is given in Table 18. The shaker results for Zn are questionable.

TABLE 17

RELEACHING SHAKER STUDY RESULTS

Coal/Leachant Ratio 0.2g/1.0g

Numbers Listed are Total Release in ppb

	DEIONIZED WATER LEACH					ACETATE BUFFER LEACH				
	48 hr	96 hr	144 hr	192 hr	288 hr	48 hr	96 hr	144 hr	192 hr	288 hr
As	1.7	2.2	3.0	3.5	3.9	3.8	4.8	7.6	11.3	15.4
Ba	48	124	120	124	132	582	997	2135	4002	5537
Cd	0.6	1.1	1.6	1.6	1.8	1.6	4.3	4.7	5.2	5.9
Cr	0.3	1.1	1.3	2.0	2.1	0.3	0.9	1.1	1.1	1.2
Co	0.2	0.6	0.8	0.9	1.3	1.1	2.3	3.5	4.8	5.4
Cu	1.3	2.5	3.0	3.4	3.8	3.0	3.5	5.6	5.6	11.0
Pb	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mn	1.3	2.5	3.0	3.4	3.8	80.0	116	232	324	410
Mo	0.7	1.4	3.0	3.6	4.7	5.1	9.0	16.8	19.0	21.1
Se	1.0	1.8	6.6	5.6	5.6	6.0	5.8	5.6	5.6	5.6
V	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Zn	35	408	342	346	348	8	116	109	107	116

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TABLE 18

COMPARISON OF THE SHAKER RELEACHING STUDY
WITH THE CONTINUOUS FLOW RELEACHING STUDY

192 HOUR VALUES (TOTAL RELEASE IN ppb).

	Deionized Water		Acetate Buffer	
Metal	Shaker	Continuous Flow (Ave.)	Shaker	Continuous Flow (Ave.)
As	3.5 ppb	3.0 ppb	11.3 ppb	25.1 ppb
Ba	124	54.4	4002	5748
Cd	1.6	1.9	5.2	4.3
Cr	2.0	0.7	1.1	2.5
Co	0.9	0.8	4.8	4.9
Cu	3.4	8.1	5.6	4.8
Pb	0	0.15	0	0
Mn	3.4	2.5	324	527
Mo	3.6	2.8	19	32.7
Se	5.6	6.6	5.6	1.2
V	0	0	0	0
Zn	(346)	6.25	(107)	4.65

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RELEACHING FACTORIAL STUDY

Experimental

A five-factor multivariate analysis on metal ion mobility in coal samples was performed. Levels of the variables and the types of controlled variables were as listed in Table 19.

TABLE 19. VARIABLES FOR RELEACHING FACTORIAL STUDY

Variable	Symbol	Level 1	Level 2	Level 3
Coal	C	Western #2	Eastern	---
Water Leachant	W	Deionized	Lake Water	---
Gas (atmosphere)	G	N_2	O_2	---
Time (hours)	H	24 hr	48 hr	---
Number of Leaches	L	1st Leach	2nd Leach	3rd Leach

The previous factorial analysis had determined the general effects of temperature, rate of circulation of leachant and particle size of the coal samples. These variables have significant effects, but not of extremely large magnitude. Therefore, these variables were eliminated from this study. Temperature was maintained at 37°C, while leachant was circulated through the 0.500-1.00 mm coal at a constant flow rate of 40 ml/min. Self-buffering actions of the coals were allowed to control the pH of the systems. This was done to approximate the behavior to be expected under industrial handling and storage.

Procedure

A charge of 200 grams of 0.500-1.00 mm sized coal and 1000 ml of leachate was placed in the continuous flow system. The leachant was allowed to circulate for a period of 24 hours, at which time a 100 ml sample was withdrawn and an equal volume replaced as previously described. At 48 and 96 hours, 800 ml of leachate were removed and replaced with fresh charges of leachant. Samples were taken at 72 and 120 hours using the same procedure as for the 24 hour samples.

The samples which were removed from the system were split into two portions. One portion was used to determine the current pH level of the circulating fluid. The other portion was filtered with suction through a 0.45 micron membrane filter and the filtered sample was stabilized with nitric acid. A separate portion of the filtered sample was treated with potassium dichromate to stabilize it for later mercury analysis. As controls: Blanks

and "spiked" blanks were also run under the same experimental conditions.

Analyses were performed for all metals involved in the study, including mercury, by flameless atomic absorption spectrophotometry.[1, 2, 10, 11, 15, 16]

Results and Discussion

The data from the lake water leached runs is not considered reliable enough to report. The experimental plan was to use fresh lake water for each run, thus reducing any effects of laboratory storage. Also, the lake water was not filtered because particulate matter was considered a natural part of the medium. Unfortunately, the different samples of lake water showed very wide variations in metal content which precluded any reasonable analysis of the data.

The results of the deionized water runs are given in Tables 20 and 21. The data were analyzed on a PDP 11/70 computer using "ANOVAR" (a library supplied analysis of variance program). Detailed results, by metal, are as follows:

Arsenic - Western Coal No. 2: There were no significant variables. The raw data were below detection limits.

Eastern Coal: Significant variables were:

L	$\alpha<0.005$
G	$\alpha<0.01$
HL	$\alpha<0.05$

Barium - Western Coal No. 2: There were no significant variables. The raw data were below detection limits.

Eastern Coal: Significant variables were:

G	$\alpha<0.01$
L	$\alpha<0.10$

Cadmium - Western Coal No. 2: There were no significant variables.

Grand Mean = 0.33 ppb; s = 0.15 ppb

Eastern Coal: There were no significant variables.

Grand Mean = 3.94 ppb; s = 0.64 ppb

Chromium - Western Coal No. 2: There were no significant variables. The raw data were below detection limits.

Eastern Coal: Significant variables were:

G	$\alpha<0.0025$
LG	$\alpha<0.10$

TABLE 20

Releaching Factorial Western #2 Coal Deionized Water Leaching

Levels				Total Release Concentrations in ppb													
H	L	G	pH	As	Ba	Cd	Cr	Co	Cu	Pb	Mn	Hg	Mo	Ni	Se	V	Zn
1	1	1	7.62	0.50	5.0	0.70	0.10	0.0	2.40	0.0	2.60	0.06	0.00	2.0	0.0	0.0	2.0
2	1	1	7.48	0.05	2.5	0.27	0.21	0.0	1.54	0.0	0.36	0.15	0.60	0.2	0.0	0.0	6.2
1	2	1	7.91	0.05	2.1	0.33	0.17	0.0	3.28	0.0	0.44	3.98*	0.48	1.2	0.0	0.0	10.0
2	2	1	7.62	0.05	2.1	0.34	0.17	0.0	3.88	0.0	0.35	0.51	1.08	1.3	0.0	0.0	13.5
1	3	1	8.02	0.05	2.1	0.42	0.17	0.1	5.40	0.0	0.35	0.51	0.96	1.1	0.0	0.0	12.9
2	3	1	8.30	0.05	2.1	0.33	0.17	0.2	5.01	0.0	0.35	0.51	0.96	3.1	1.0	0.0	13.0
1	1	2	7.64	0.50	2.0	0.10	0.10	0.0	1.50	0.0	0.10	--	0.50	0.0	1.0	3.0	1.0
2	1	2	7.59	0.05	4.2	0.11	0.11	0.0	2.85	0.0	1.91	--	0.95	2.0	0.1	16.3	1.1
1	2	2	7.80	0.05	3.4	0.29	0.09	0.0	3.91	0.10	5.33	--	1.27	1.6	0.1	36.1	1.9
2	2	2	7.78	0.55	5.4	0.31	0.19	0.0	5.47	0.41	2.31	--	1.32	4.6	0.1	28.5	2.0
1	3	2	7.77	0.95	7.0	0.37	0.27	0.0	6.27	0.33	2.33	--	1.22	4.0	0.1	27.9	3.8
2	3	2	7.84	0.50	5.2	0.38	0.18	0.0	6.21	0.33	2.44	--	1.62	6.0	2.1	30.1	3.0

TABLE 21

Releaching Factorial Eastern Coal Deionized Water Leaching

Levels			pH	Total Release Concentrations in ppb												
H	L	G		As	Ba	Cd	Cr	Co	Cu	Pb	Mn	Hg	Mo	Ni	Se	V	Zn
1	1	1	3.23	0.00	43.0	4.20	1.10	106	9.30	0.20	700	0.38	0.0	210	0.0	0.0	220
2	1	1	3.31	0.00	36.4	3.92	0.51	109	6.44	0.02	732	0.35	0.0	191	0.0	0.0	143
1	2	1	3.60	0.50	34.0	3.72	0.43	110	8.44	0.02	727	0.32	0.0	187	1.0	0.0	169
2	2	1	3.61	0.05	39.4	3.77	0.43	107	9.16	0.02	756	0.29	0.0	206	0.1	0.0	151
1	3	1	3.80	0.55	42.6	4.07	0.43	111	12.9	0.02	788	0.33	0.0	213	1.1	0.0	155
2	3	1	3.90	0.60	46.1	4.01	0.43	115	13.9	0.02	810	0.42	0.0	218	2.2	0.0	155
1	1	2	3.52	1.00	22.0	2.30	1.00	107	14.2	0.10	830	--	0.0	180	0.0	0.0	65
2	1	2	3.28	1.10	26.2	3.43	1.10	114	24.0	0.01	1150	--	0.0	238	0.0	0.0	137
1	2	2	3.21	1.90	35.4	4.79	1.00	123	38.6	0.11	1170	--	0.0	254	2.0	0.0	151
2	2	2	3.18	1.50	31.9	4.19	1.71	141	47.2	0.22	1180	--	0.0	281	2.2	0.0	152
1	3	2	3.27	1.40	35.1	4.25	1.55	147	50.9	0.18	1230	--	0.0	300	1.8	0.0	162
2	3	2	3.08	1.90	37.6	4.68	1.95	150	63.9	0.18	1300	--	0.0	323	1.8	0.0	184

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Cobalt - Western Coal No. 2: There were no significant variables. The raw data were below detection limits.

Eastern Coal: Significant variables were:

G	$\alpha<0.01$
L	$\alpha<0.05$
LG	$\alpha<0.10$

Copper - Western Coal No. 2: Significant variables were:

L	$\alpha<0.001$
G	$\alpha<0.025$

Eastern Coal: Significant variables were:

L	$\alpha<0.001$
G	$\alpha<0.001$
LG	$\alpha<0.001$
HG	$\alpha<0.005$
H	$\alpha<0.01$

Lead - Western Coal No. 2: G was significant with $\alpha<0.10$ but all but one raw data point out of twelve were below single point detection limits.

Eastern Coal: The statistics were confused and only two out of twelve raw data points were above detection limits.

Manganese - Western Coal No. 2: The only significant variable was G at $\alpha<0.10$. The mean, total releases from N_2 and O_2 are:

0.74 ppb for N_2
2.40 ppb for O_2

Eastern Coal: Significant variables were:

G	$\alpha<0.001$
L	$\alpha<0.10$

Mercury - Only the N_2 run for mercury was analyzed. With the exception of one sample which seemed to be obviously contaminated, the Hg concentrations were quite low. No significant trends appeared.

Molybdenum - Western Coal No. 2: The variables H, L and G showed high significance but the raw data were below single point detection limits.

Eastern Coal: All Mo concentrations were zero.

Nickel - Western Coal No. 2: Significant variables were:

G	$\alpha<0.10$
L	$\alpha<0.10$

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Eastern Coal: Significant variables were:

G $\alpha<0.01$
L $\alpha<0.10$

Selenium - Western Coal No. 2: There were no significant variables and the mean was below detection limits. No plot was made.

Eastern Coal: The only significant variable was L with $\alpha<0.01$. There was a reasonable but not significant G effect. The raw data were very near single point detection limits.

Vanadium - Western Coal No. 2: Significant variables were:

G $\alpha<0.001$
L $\alpha<0.025$
LG $\alpha<0.025$

The data for N_2 were all zero.

Eastern Coal: All V concentrations were zero.

Zinc - Western Coal No. 2: Significant variables were:

G $\alpha<0.001$
L $\alpha<0.01$
LG $\alpha<0.05$

Eastern Coal: There were no significant variables. The total release grand mean for Zn was 154 ppb.

General Discussion of Results

The most obvious result of these runs is the fact that Western Coal No. 2 showed very different leaching behavior than Western Coal No. 1. Specifically, comparing these results with the results for the continuous flow re-leaching runs (done on Western Coal No. 1) one sees that there was much more leachable metal in Western Coal No. 1. No control of or knowledge of the actual mine sites were available for this work. The most probable assumption is that the Western Coal No. 2 sample was taken from an aquifer vein and was thus already thoroughly leached. The EDTA runs also clearly show this comparison between the two samples of western coal.

For the few metals which show significant leaching from the western coal, both gas saturation and number of releachings show significant effects. All metals except zinc show increased leaching with oxygen saturation.

The Western Coal No. 2 also seems to show somewhat higher pH values in the leachate than Western Coal No. 1. This could, of course, be caused by alkaline water in the aquifer.

The Eastern Coal shows higher concentrations in the leachate for all metals except molybdenum and vanadium. The pH of the leachate from eastern coal is much lower than leachate from the western coals. These effects are as expected.

Oxygen saturation increases leaching in the Eastern Coal in all cases except barium.

Overall, the following trends emerge:

1. Eastern Coal is acidic and leaches more metals than western coal.
2. There are pronounced differences between different samples of western coal.
3. Oxygen enhances leaching in most cases.

EDTA SHAKER STUDY

Experimental

The purpose of this study was to determine the amount of metal mobilized by a leachant of high sequestering power. A leachant with high sequestering ability could be capable of a more vigorous competition with complexing sites on the coal matrix and thus give an indication of the amount of metal which could ultimately be removed by very prolonged leaching with leachants of lower complexing power.

A 0.01 M solution of ethylenediaminetetraacetic acid, di-sodium salt (EDTA) was prepared using deionized water as a solvent, and the pH of the resulting EDTA solution was adjusted to an appropriate level by the use of either ultrapure nitric acid or sodium hydroxide. pH levels of 7.5 and 3.4 were used in this experiment.

These hydrogen ion concentrations were chosen because the self-buffering action of the western coals resulted in an alkaline solution when deionized water was used as a leachant, while the eastern coal sample produced a distinctly acidic system. By pre-setting the pH of the EDTA leachant, it was felt that any effect would be due to the initial sequestering ability of the leachant, rather than to self-titration of the coal-disodium EDTA mixture.

One hundred ml of the EDTA solution which had been adjusted to pH 7.5 was added to separate 20.0 gram samples of Western Coals No. 1 and No. 2.

The coal sample and EDTA solution were placed into a 125 ml polyprophlene bottle. In a similar manner, 100 ml of EDTA solution (adjusted to pH 3.4) was added to 20.0 grams of eastern coal. Coal samples were in the 0.500-1.00 mm size range. All three types of samples were run in duplicate.

The coal-EDTA mixtures were placed in a constant temperature shaker bath and were allowed to shake for 48 hours at a temperature of approximately 40°C. The shaking rate was one oscillation of the sample platform per second. Sample platform travel was 28 mm.

After 48 hours, the pH of an unfiltered portion of each sample was determined and the remaining portion of the sample was filtered through a 0.45 micron membrane filter, using an all-plastic construction suction filtration

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apparatus. After filtration, the samples were acidified to stabilize them, and the metal concentrations were determined by flameless atomic absorption spectrophotometry.[1, 2, 11, 15, 16]

One hundred ml portions of the high and low pH adjusted EDTA solutions were shaken along with the coal-EDTA samples and used as control blanks in the analyses. All metals except mercury were determined.

Results and Discussion

The initial observation is that the EDTA-coal systems shifted pH to more acid levels. See Table 21. This would, of course, be expected from reactions such as:

$$H_2Y^{2-} + M^{2+} \longrightarrow YM^{2-} + 2H^+$$

where Y^{4-} is the completely ionized EDTA ion and M^{2+} is any di-positive metal ion. Because the initial pH levels were set to the natural, buffered levels of coal-deionized water systems, these observed shifts demonstrate that a significant amount of EDTA complexation took place in the system.

The pH shift also makes interpretation of the data more difficult because of the dependence of metal leaching on pH.

The leachate analyses for the EDTA runs are shown in Table 22. This table also lists analyses for comparable non-EDTA runs.

Examination of the results shows that EDTA extracts significantly more metal ion from the coal than pure deionized water with the exceptions of: (a) a strong reversal for cobalt in the Eastern Coal and (b) a possibly reversed value for selenium in the Western Coal No. 1. Strong evidence that the effect is not due to pH alone is given by the comparison between EDTA runs and the acetate buffered run for Western Coal No. 1. Here, the comparison run has a lower final pH than the EDTA runs and yet the metal extraction is still significantly higher for the EDTA runs than for the comparison run.

From an environmental viewpoint, it would appear that there could be significant amounts of heavy metal mobilization with strong complexing agents.

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TABLE 22

LEACHATE ANALYSIS FOR EDTA RUNS AND VALUES FOR COMPARABLE NON-EDTA RUNS

Coal	Western #1			Western #2			Eastern
Run Designation	Shaker Run With Water Deionized	Shaker Run With Acetate Buffer	EDTA Runs (Average of 2 Runs)	Continuous Flow Run With Water Deionized	EDTA Runs (Average of 2 Runs)	Continuous Flow Run With Water Deionized	EDTA Runs
Initial pH			7.51		7.51		3.41
Final pH	7.23	7.74	5.56	7.48	6.11	3.31	2.66
Metals							
As	1.7	3.8	5.1	0.0	0.5	0.0	140
Ba	40	582	405	3	425	32	110
Cd	0.6	1.6	2.6	0.15	1.0	3.5	2.8
Cr	0.3	0.3	(3.6)	0.1	1.1	0.4	18
Co	0.2	1.1	19.6	0.0	10.0	98	13.7
Cu	4.2	3.0	135	1.5	70	5.5	200
Pb	0	0	62	0.0	30	0	70
Mn	1.3	80	1250	0.1	950	660	1130
Mo	0.7	5.1	4	0.6	1	0	12
Ni	5*	5*	65	0.5	40	170	285
Se	1	6	(0.8)	0.0	0.2	0	3.0
V	0	0	50	0.0	10	0	10
Zn	35	8	53	6	29	120	225

Values in parenthesis are doubtful because of high blanks.

*Approximate values from 1st factorial run.

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SPIKED SYSTEM UPTAKE STUDY

This experiment investigated the uptake of metal ions by the system (coal, system walls, etc.) by spiking the leachant with several different concentrations of added metal ions.

Experimental

Three different types of solutions were used. They were:

1. Deionized water (3 spiking levels)
2. Lake Superior water (2 spiking levels)
3. Prepared coal leachate (5 spiking levels)

A set of metal ion concentrations was adapted (see Table 23) which approximated, in magnitude, the concentration levels found in the preceeding deionized water experiments. Spiking levels are reported as mulpitles of these, base level, concentrations.

The "prepared coal leachate" was obtained by shaking Western Coal No. 2 and deionized water in the ratio: 1 gram of coal to 5 ml water. The coal was shaker leached for 64 hours. The leachate was filtered two times through 0.45 μ membrane filters before use.

Some runs were made with spiked, leachate and coal in the ratio: 1 gram coal to 5 ml of spiked leachate.

In addition, 250 ml of leachate alone and 250 ml of leachate with 7.5 grams of small pieces of silicone tubing were shaken in polypropylene bottles in the mechanical shaker bath for 48 hours.

The continuous flow runs were sampled at 6, 24 and 48 hours.

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TABLE 23

BASE LEVEL SPIKING CONCENTRATIONS

Metal	Concentration (ppb)	Metal	Concentration (ppb)
Arsenic	2	Manganese	20
Barium	100	Molybdenum	20
Cadmium	2	Nickel	20
Chromium	10	Selenium	2
Cobalt	10	Vanadium	50
Copper	10	Zinc	10
Lead	5		

Results and Discussion

The results of the spiked system uptake study are presented in Tables 24 through 36. The prepared leachate 3 X* run is rejected from further consideration because (a) it shows a reverse pH effect and (b) the results are in complete disagreement with the other runs for many of the metals.

Consider first the system uptake from spiked, deionized water. Having no buffer capacity, these runs had a fairly large pH drop, probably due to atmospheric carbon dioxide. Consequently, comparisons with the other runs are probably not significant.

In order to get a better visualization of the various metal uptakes, Table 37 has been constructed. Here, an "uptake ratio" equal to the initial concentration divided by the 48 hour concentration has been listed for each metal at 3 X and 9 X for the three systems of interest. A large value of the uptake ratio signifies a large portion of the metal absorbed by the system and lost to analysis.

In the lake water and prepared leachate systems, the metal losses would be due either to adsorption on the system walls or loss in final filtration. The final filtration loss could be due either to an adsorption on the filter or the coagulation of particles which would be retained by the filter. No systematic attempt was made to separate these effects in this work.

In the coal plus leachate system, any losses in addition to the above should be due to direct sequestering by the coal itself.

The first fact to be derived from Table 37 is that a highly significant

amount of metal ion is usually absorbed by the coal, and significant amounts of metal are lost to the system in most cases. A rough estimate of losses to the walls and/or final filter at pH $\simeq$ 7.3 would be from zero to about 60% except for lead and cadmium where these losses are much larger. A study to separate the wall and filter effects at slightly basic pH values would seem to have a highly priority in any future work.

It appears that an equilibrium is established between the various parts of the system and that in a real leaching situation, the absorptive property of the coal itself is almost always the controlling factor. If one compares this section of the study with the releaching work, the coal titration studies and the EDTA experiments, the following picture emerges: Any single pass of metal free, aqueous leachant through western coal should quickly assume a pH slightly above 7.0 and will transfer some metals from the coal. The concentrations of these metals should be well below current EPA limits. Continuous leaching using continuously supplied fresh leachant would add much larger amounts of heavy metals to the environment.

Some attempts were made to fit the data to an equilibrium mechanism. Due to the limited data and possibly due to the general complexity of the system, the mathematical fits were sporadic at best and are not reported here.

TABLE 24

SPIKED SYSTEM UPTAKE STUDY

ARSENIC

Nominal Spiking Level: X = 2 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	15	7.66	18	18	21	5.87
		9 X	63	7.62	42	48	40	5.69
	Lake Water	3 X	12	7.64	12	12	13	7.50
		9 X	35	7.68	30	25	35	7.56
	Prepared Leachate	0 X	0	7.60	0	0	0	7.21
		1 X	4.0	7.64	1.5	1.5	3.0	7.34
		3 X*	8.5	7.62	9.5	8.5	10.0	7.80
		3 X	8.5	7.62	6.0	8.0	8.0	7.55
		9 X	40	7.57	30	40	30	6.98
		27 X	110	7.64	90	90	110	6.92
	Leachate Plus Coal	3 X	11.0	7.48	5.5	1.5	2.0	6.99
		9 X	40	7.58	20	7.5	5.5	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	1.0	7.41	----	----	0.5	----
		1 X	3.0	7.49	----	----	3.5	----
	Leachate Plus Silicone Tubing	0 X	1.0	7.41	----	----	0.0	7.20
		1 X	3.0	7.49	----	----	3.0	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 25

SPIKED SYSTEM UPTAKE STUDY

BARIUM

Nominal Spiking Level: X = 100 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	240	7.66	260	280	305	5.87
		9 X	790	7.62	850	850	900	5.69
	Lake Water	3 X	400	7.64	400	450	450	7.50
		9 X	----	7.68	----	----	----	7.56
	Prepared Leachate	0 X	6	7.60	2	2	2	7.21
		1 X	100	7.64	70	35	30	7.34
		3 X*	240	7.62	35	15	12	7.80
		3 X	240	7.62	100	110	75	7.55
		9 X	870	7.57	620	470	450	6.98
		27 X	2570	7.64	690	400	330	6.92
	Leachate Plus Coal	3 X	340	7.48	15	16	18	6.99
		9 X	1300	7.58	80	65	75	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	7	7.41	----	----	5	----
		1 X	140	7.49	----	----	95	----
	Leachate Plus Silicone Tubing	0 X	7	7.41	----	----	5	7.20
		1 X	140	7.49	----	----	95	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 26

SPIKED SYSTEM UPTAKE STUDY

CADMIUM

Nominal Spiking Level: X = 2 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	5.0	7.66	5.3	5.0	6.1	5.87
		9 X	15.4	7.62	14.1	12.7	15.4	5.69
	Lake Water	3 X	3.6	7.64	3.0	2.5	2.2	7.50
		9 X	14.0	7.68	11.0	7.0	6.0	7.56
	Prepared Leachate	0 X	0	7.60	0.0	0.1	1.5	7.21
		1 X	1.3	7.64	0.2	0.2	1.5	7.34
		3 X*	4.9	7.62	0.3	0.1	0.0	7.80
		3 X	4.9	7.62	0.7	0.4	0.4	7.55
		9 X	10.8	7.57	4.6	2.0	3.7	6.98
		27 X	65	7.64	7.0	0.8	3.3	6.92
	Leachate Plus Coal	3 X	3.4	7.48	0	0	0	6.99
		9 X	11.5	7.58	0	0	0.1	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	0.8	7.41	----	----	0	----
		1 X	2.2	7.49	----	----	0.9	----
	Leachate Plus Silicone Tubing	0 X	0.8	7.41	----	----	0	7.20
		1 X	2.2	7.49	----	----	0.9	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 27

SPIKED SYSTEM UPTAKE STUDY

CHROMIUM

Nominal Spiking Level: X = 10 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	24	7.66	19	18	17	5.87
		9 X	90	7.62	60	55	50	5.69
	Lake Water	3 X	25	7.64	25	20	20	7.50
		9 X	95	7.68	85	45	40	7.56
	Prepared Leachate	0 X	0.1	7.60	0.0	0.3	0.0	7.21
		1 X	12.9	7.64	6.7	5.4	6.5	7.34
		3 X*	31	7.62	30	23	25	7.80
		3 X	31	7.62	25	23	21	7.55
		9 X	80	7.57	65	55	55	6.98
		27 X	290	7.64	270	190	230	6.92
	Leachate Plus Coal	3 X	29	7.48	9.1	2.7	0.9	6.99
		9 X	85	7.58	29	2.2	0.9	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	0.1	7.41	----	----	0.1	----
		1 X	8.5	7.49	----	----	8.4	----
	Leachate Plus Silicone Tubing	0 X	0.1	7.41	----	----	0.1	7.20
		1 X	8.5	7.49	----	----	8.3	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 28

SPIKED SYSTEM UPTAKE STUDY

COBALT

Nominal Spiking Level: X = 10 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb)			48 hr Sample pH
					6 hr	24 hr	48 hr	
Continuous Flow Leaching Columns	Deionized Water	3 X	23	7.66	23	24	27	5.87
		9 X	90	7.62	90	90	90	5.69
	Lake Water	3 X	27	7.64	28	22	27	7.50
		9 X	100	7.68	90	75	65	7.56
	Prepared Leachate	0 X	0	7.60	0	0	0	7.21
		1 X	8.8	7.64	3.2	1.7	1.2	7.34
		3 X*	30	7.62	5.2	2.5	1.4	7.80
		3 X	30	7.62	13.7	12.0	10.6	7.55
		9 X	90	7.57	65	45	45	6.98
		27 X	320	7.64	120	70	30	6.92
	Leachate Plus Coal	3 X	27	7.48	0	0	0	6.99
		9 X	105	7.58	1.7	1.1	0.9	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	0	7.41	----	----	0	----
		1 X	7.8	7.49	----	----	8.5	----
	Leachate Plus Silicone Tubing	0 X	0	7.41	----	----	0	7.20
		1 X	7.8	7.49	----	----	8.4	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 29

SPIKED SYSTEM UPTAKE STUDY

COPPER

Nominal Spiking Level: X = 10 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	18	7.66	23	22	23	5.87
		9 X	75	7.62	70	70	70	5.69
	Lake Water	3 X	30	7.64	18	19	13	7.50
		9 X	85	7.68	50	25	10	7.56
	Prepared Leachate	0 X	2.5	7.60	0.5	5.5	1.3	7.21
		1 X	10	7.64	3.0	6.5	4.2	7.34
		3 X*	26	7.62	4.0	8.0	4.0	7.80
		3 X	26	7.62	11	10	10	7.55
		9 X	80	7.57	35	25	20	6.98
		27 X	245	7.64	65	20	10	6.92
	Leachate Plus Coal	3 X	27	7.48	6.0	5.0	3.0	6.99
		9 X	95	7.58	5.0	4.0	3.0	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	1.0	7.41	----	----	2.0	----
		1 X	11	7.49	----	----	6.0	----
	Leachate Plus Silicone Tubing	0 X	1.0	7.41	----	----	4.0	7.20
		1 X	11	7.49	----	----	13	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 30

SPIKED SYSTEM UPTAKE STUDY

LEAD

Nominal Spiking Level: X = 5 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	8.0	7.66	7.0	7.4	8.1	5.87
		9 X	30	7.62	19	19	21	5.69
	Lake Water	3 X	7.8	7.64	5.0	4.6	2.3	7.50
		9 X	30	7.68	20	2.0	0.9	7.56
	Prepared Leachate	0 X	0	7.60	0	0	0	7.21
		1 X	1.6	7.64	0.2	0.0	0.1	7.34
		3 X*	7.1	7.62	0.6	2.3	0.2	7.80
		3 X	7.1	7.62	0.7	0.3	0.3	7.55
		9 X	30	7.57	8.0	3.0	1.9	6.98
		27 X	80	7.64	60	30	25	6.92
	Leachate Plus Coal	3 X	8.0	7.48	0.5	0.2	0.2	6.99
		9 X	25	7.58	0.0	0.2	0.1	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	0.1	7.41	----	----	0.3	----
		1 X	2.5	7.49	----	----	1.5	----
	Leachate Plus Silicone Tubing	0 X	0.1	7.41	----	----	0.3	7.20
		1 X	2.5	7.49	----	----	1.2	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 31

SPIKED SYSTEM UPTAKE STUDY

MANGANESE

Nominal Spiking Level: X = 20 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	50	7.66	45	47	50	5.87
		9 X	150	7.62	135	130	145	5.69
	Lake Water	3 X	60	7.64	47	60	38	7.50
		9 X	150	7.68	140	107	95	7.56
	Prepared Leachate	0 X	0.7	7.60	0.1	0.6	0.1	7.21
		1 X	18.3	7.64	5.6	3.8	3.4	7.34
		3 X*	50	7.62	11.1	4.6	2.4	7.80
		3 X	50	7.62	27	17.2	18.1	7.55
		9 X	150	7.57	105	85	80	6.98
		27 X	470	7.64	230	100	60	6.92
	Leachate Plus Coal	3 X	55	7.48	0.4	0.4	0.3	6.99
		9 X	195	7.58	5.5	2.2	2.3	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	0.8	7.41	----	----	0.5	----
		1 X	18.4	7.49	----	----	15.2	----
	Leachate Plus Silicone Tubing	0 X	0.8	7.41	----	----	0.3	7.20
		1 X	18.4	7.49	----	----	16.4	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 32

SPIKED SYSTEM UPTAKE STUDY

MOLYBDENUM

Nominal Spiking Level: X = 20 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	50	7.66	50	55	60	5.87
		9 X	180	7.62	160	180	150	5.69
	Lake Water	3 X	105	7.64	105	100	100	7.50
		9 X	200	7.68	250	240	210	7.56
	Prepared Leachate	0 X	0	7.60	0	0	0	7.21
		1 X	12	7.64	12	9	11	7.34
		3 X*	60	7.62	35	45	50	7.80
		3 X	60	7.62	45	45	50	7.55
		9 X	120	7.57	150	120	160	6.98
		27 X	530	7.64	540	430	490	6.92
	Leachate Plus Coal	3 X	63	7.48	40	42	40	6.99
		9 X	160	7.58	130	110	100	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	0.4	7.41	----	----	0.0	----
		1 X	11.1	7.49	----	----	9.2	----
	Leachate Plus Silicone Tubing	0 X	0.4	7.41	----	----	0.0	7.20
		1 X	11.1	7.49	----	----	9.2	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 33

SPIKED SYSTEM UPTAKE STUDY

NICKEL

Nominal Spiking Level: X = 20 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb)			48 hr Sample pH
					6 hr	24 hr	48 hr	
Continuous Flow Leaching Columns	Deionized Water	3 X	67	7.66	58	53	53	5.87
		9 X	170	7.62	150	170	150	5.69
	Lake Water	3 X	60	7.64	47	60	38	7.50
		9 X	150	7.68	140	107	95	7.56
	Prepared Leachate	0 X	1	7.60	1	3	0	7.21
		1 X	17	7.64	17	11	15	7.34
		3 X*	46	7.62	11	11	7	7.80
		3 X	46	7.62	34	38	25	7.55
		9 X	210	7.57	160	160	110	6.98
		27 X	600	7.64	450	110	70	6.92
	Leachate Plus Coal	3 X	46	7.48	3	2	4	6.99
		9 X	170	7.58	9	3	4	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	1	7.41	----	----	1	----
		1 X	17	7.49	----	----	19	----
	Leachate Plus Silicone Tubing	0 X	1	7.41	----	----	3	7.20
		1 X	17	7.49	----	----	17	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 34

SPIKED SYSTEM UPTAKE STUDY

SELENIUM

Nominal Spiking Level: X = 2 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb)			48 hr Sample pH
					6 hr	24 hr	48 hr	
Continuous Flow Leaching Columns	Deionized Water	3 X	7	7.66	6	7	5	5.87
		9 X	20	7.62	20	19	20	5.69
	Lake Water	3 X	9	7.64	6	9	8	7.50
		9 X	19	7.68	20	21	20	7.56
	Prepared Leachate	0 X	0	7.60	0	0	0	7.21
		1 X	2	7.64	2	0	2	7.34
		3 X*	6	7.62	6	5	3	7.80
		3 X	6	7.62	6	5	3	7.55
		9 X	19	7.57	14	16	14	6.98
		27 X	60	7.64	60	60	50	6.92
	Leachate Plus Coal	3 X	8	7.48	6	5	0	6.99
		9 X	21	7.58	13	4	2	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	0	7.41	----	----	0	----
		1 X	3	7.49	----	----	0	----
	Leachate Plus Silicone Tubing	0 X	0	7.41	----	----	0	7.20
		1 X	3	7.49	----	----	2	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 35

SPIKED SYSTEM UPTAKE STUDY

VANADIUM

Nominal Spiking Level: X = 50 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	190	7.66	150	150	190	5.87
		9 X	750	7.62	550	700	650	5.69
	Lake Water	3 X	240	7.64	210	230	250	7.50
		9 X	650	7.68	850	650	700	7.56
	Prepared Leachate	0 X	3	7.60	0	0	0	7.21
		1 X	80	7.64	45	25	30	7.34
		3 X*	200	7.62	160	190	160	7.80
		3 X	200	7.62	160	180	180	7.55
		9 X	750	7.57	550	600	600	6.98
		27 X	2200	7.64	1900	1650	1800	6.92
	Leachate Plus Coal	3 X	240	7.48	70	30	15	6.99
		9 X	850	7.58	150	70	35	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	0	7.41	----	----	0	----
		1 X	70	7.49	----	----	85	----
	Leachate Plus Silicone Tubing	0 X	0	7.41	----	----	0	7.20
		1 X	70	7.49	----	----	85	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 36

SPIKED SYSTEM UPTAKE STUDY

ZINC

Nominal Spiking Level: X = 10 ppb

Leaching System	Concentration	Nominal Spiking Level	Measured Initial Concentration (ppb)	Initial pH	Sample Concentrations (ppb) 6 hr	24 hr	48 hr	48 hr Sample pH
Continuous Flow Leaching Columns	Deionized Water	3 X	15	7.66	15	15	15	5.87
		9 X	55	7.62	50	55	55	5.69
	Lake Water	3 X	15	7.64	7.0	7.0	5.0	7.50
		9 X	50	7.68	40	20	20	7.56
	Prepared Leachate	0 X	1.1	7.60	0.3	1.3	0.9	7.21
		1 X	8.7	7.64	1.3	8.2	1.5	7.34
		3 X*	16	7.62	4.0	4.2	3.2	7.80
		3 X	16	7.62	7.2	17	12	7.55
		9 X	55	7.57	20	20	15	6.98
		27 X	160	7.64	45	35	15	6.92
	Leachate Plus Coal	3 X	22	7.48	1.4	1.2	0.9	6.99
		9 X	80	7.58	1.3	1.4	3.4	6.81
Polypropylene Bottles in Shaker Bath	Leachate	0 X	1.4	7.41	----	----	1.4	----
		1 X	5.5	7.49	----	----	5.5	----
	Leachate Plus Silicone Tubing	0 X	1.4	7.41	----	----	1.5	7.20
		1 X	5.5	7.49	----	----	6.2	7.17

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE 37

$$\text{UPTAKE RATIO} = \frac{\text{INITIAL CONCENTRATION}}{\text{FINAL CONCENTRATION}}$$

	Lake Water		Prepared Leachate		Leachate and Coal	
Metal	3 X	9 X	3 X	9 X	3 X	9 X
As	0.92	1.0	1.1	1.3	5.5	7.3
Ba	0.89	---	3.2	1.9	19	17
Cd	1.6	2.3	12	2.9	∞	115
Cr	1.3	2.4	1.5	1.5	32	94
Co	1.0	1.5	2.8	2.0	∞	117
Cu	2.3	8.5	2.6	4.0	9.0	32
Pb	3.4	30	24	16	40	250
Mn	1.6	1.6	2.8	1.9	183	85
Mo	1.1	0.95	1.2	0.75	1.6	1.6
Ni	1.6	1.6	1.8	1.9	12	43
Se	1.1	0.95	2.0	1.4	∞	11
V	0.96	0.93	1.1	1.3	16	24
Zn	3.0	2.5	1.3	3.7	24	24

SHORT TERM SHAKER STUDY

Throughout this work, metal analyses at very short times showed wild fluctuations with initial spikes. This experiment was done to confirm this effect.

Experimental

Six 125 ml polypropylene bottles, each containing 15.0 grams of 0.500-1.00 mm sized Western Coal No. 2 and 75 ml of deionized water were placed in a constant temperature shaker bath. The samples were maintained at a temperature of 40°C and were shaken gently at a cycle rate of approximately 45 oscillation per minute for the specified lengths of time.

Samples were removed from analysis at the following times: 15 min, 30 min, 1 hr, 2 hr, 4 hr and 6 hr. After the removal of the sample bottle from the shaker bath at a designated time, a portion of the unfiltered leachate was removed for a determination of the pH of the leachate.

The remainder of the leachate was filtered with suction through a 0.45 micron member filter supported in an all-plastic filtration apparatus, and then acidified to a pH of approximately 2 with ultrapure nitric acid. The acidified, filtered leachate was preserved for metal analysis by flameless atomic absorption spectrophotometry. All metals except mercury were determined.

Results and Discussion

Of the metals analyzed, only barium, cadmium, cobalt, copper, manganese, nickel, selenium and zinc gave results at or above detection limits. The data for these metals are given in Table 38. Initial spikes seem to appear for all of these metals except possibly manganese and selenium. There is no adequate explanation at present for this phenomenen.

TABLE 38

SHORT TERM SHAKER RESULTS

All Concentrations in ppb

Time	15 min	30 min	1 hr	2 hr	4 hr	6 hr
pH	7.84	7.37	7.35	7.33	7.30	7.31
Ba	16 ppb	13 ppb	6 ppb	6 ppb	6 ppb	6 ppb
Cd	0.0	0.2	0.0	0.0	0.0	0.0
Co	0.3	0.6	0.3	0.4	0.0	0.1
Cu	2.3	3.6	2.3	2.7	2.1	2.1
Mn	0.2	0.3	0.3	0.7	0.2	0.3
Ni	0	1	0	0	0	0
Se	0	2	1	0	1	3
Zn	1	8	3	4	1	1

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SECTION 7

ERROR STATISTICS OF ANALYTICAL DATA

Aside from the pooled higher order interactions which were used in the analysis of variance work, some independent statistical measures of precision were needed. These statistics were calculated from three sources:

1. Duplicate atomic absorption runs were made on some of the analate solutions. These measurements, especially ones made at low metal ion concentrations, furnish excellent data for an estimation of detection limits.
2. A few analate solutions were run repeatedly in the atomic absorption spectrophotometer as a measure of relative instrumental error.
3. Certain entire runs were duplicated. These data were analyzed for an estimate of run to run variance.

The Duplicate Atomic Absorption Runs

The calculated statistics for the low level duplicates are tabulated in Table 38 where:

s = the pooled standard deviation in ppb
d.f. = the degrees of freedom
y = average ppb of metal to give 0.001 absorbance unit on the A.A. (y is listed for both unpyrolized and pyrolized furnace tubes)
s/y = the calculated ratio of s to y

The blanks in the table are explained as follows: (a) Cd was always run by standard addition so that no direct y was available, (b) Se was not analyzed in unpyrolized cells and (c) no V was found in any of the samples in this series.

The average of the s/y values from Table 39 is 1.57 which gives an average s of 1.57 y. Then $\sigma = 1.57$ y. Assuming an α probability of 0.05 gives 95% confidence limits of $1.96\sigma = 3.08$ y so that an $\alpha = 0.05$ detection limit would be about 3 x (concentration to give 0.001 A unit).

This overall estimate compares favorably with the 4 x (concentration to give 0.001 A unit) which has been used as a detection limit estimate (Ref. 1, 1973, unrevised).

These detection limit estimates are used as a basis for rejection of the data for certain metals in certain experiments where the level is too low to warrant further analysis.

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The low level detection limits are listed in Table 40.

TABLE 39

STATISTICS FOR LOW LEVEL DUPLICATE RUNS

Metal	s	d.f. (for s)	y			s/y
			Unpyrolized	Pyrolized	Weighted Average	
As	0.319	23	0.173	0.20	0.186	1.72
Ba	1.45	7	4.45	2.21	3.45	0.42
Cd	0.0267	7	--	--	--	--
Cr	0.0866	18	0.172	0.072	0.122	0.71
Co	0.463	7	0.34	0.108	0.166	2.79
Cu	0.253	24	0.152	0.096	0.124	2.04
Pb	0.248	15	0.155	0.045	0.073	3.40
Mn	0.0809	13	0.078	0.072	0.075	1.08
Mo	0.346	6	2.19	0.553	0.961	0.36
Ni	0.805	9	1.36	0.252	0.569	1.41
Se	0.339	7	--	0.31	0.31	1.09
Zn	0.127	8	0.06	0.053	0.056	2.27
V	--	--	7.85	3.02	4.23	--

TABLE 40

CALCULATED 95% (α = 0.05) DETECTION LIMITS
FOR ANALYSIS AT LOW CONCENTRATIONS

Metal	95% Detection Limits (ppb)	
	Unpyrolized	Pyrolized
As	0.52	0.60
Ba	13	6.6
Cr	0.52	0.22
Co	1.0	0.32
Cu	0.46	0.29
Pb	0.47	0.14
Mn	0.23	0.22
Mo	6.6	1.7
Ni	4.1	0.76
Se	---	0.93
V	24	9.1
Zn	0.18	0.16

Overall estimate for Cd = 0.080 ppb

Both the absolute and the relative errors found at moderate to high concentrations are different from those found at very low concentrations.

Errors at moderate concentrations were checked on three metals. The results are shown in Table 41. The relative, measurement-to-measurement standard deviations fell in the 3% to 18% range with an average of 11%. This agrees with a common rule of thumb that atomic absorption measurements are precise to about 10%.

There are, of course, extensive variations in precision depending on metal, metal concentration, age of furnace tube, dilution technique, etc.

However, such an investigation is not needed here. In general, the effects observed are either well above 10% or are based on a sufficient number of observations to reduce the error to tolerable limits.

Run-to-run variances were estimated from the continuous flow, releaching study.

These relative standard deviations between runs at each particular time were calculated using:

$$s_{\text{relative}} = \frac{s}{\bar{x}} = \left(\frac{X_2 - X_1}{\sqrt{2}}\right) \cdot \frac{2}{X_2 + X_1} = \sqrt{2} \left|\frac{X_2 - X_1}{X_2 + X_1}\right|$$

The s relative values for each metal and condition were then averaged over the four sampling times using:

$$s_{\text{relative, average}} = \left(\sum_i (s_i)^2\right)^{1/2}$$

The results are tabulated in Table 42.

Evaluating those runs which are at or near detection limits yields a pooled s_{relative} over all metals and conditions of 18.9%.

The statistical calculations are for the most part, a posteriori to the experiments and do not represent the best estimators that could be designed. Nevertheless, it is felt that values of $s_{\text{relative}} \tilde{=} 10\%$ for A.A. analyses and $s_{\text{relative}} \tilde{=} 20\%$ for overall run to run results are reasonable estimates of experimental precision when the data is well above detection limits.

TABLE 41

RELATIVE ANALYTICAL ERRORS AT MODERATE CONCENTRATIONS

Metal	Number Measurements	$\bar{x}$	s	Relative Error $z/\bar{x}$%
Pb	9	3.71	0.33	9.0
	8			
Ba	8	178	27.3	15.4
	8	135	24.3	18.0
Mn	8	9.60	0.293	3.0
	8	18.0	0.667	3.7

TABLE 42

RUN TO RUN RELATIVE STANDARD DEVIATIONS FOR CONTINUOUS FLOW RELEACHING STUDIES

Metal	Mean $s_{relative}$ in %	
	Millipore Water Runs (%)	Acetate Buffer Runs (%)
As	5.10	1.53
Ba	6.63	4.88
Cd	16.5	11.5
Cr	32.0*	14.6
Co	0.0*	5.63
Cu	7.03	42.4
Mn	29.3	7.29
Mo	15.4	2.81
Se	27.9	49.7*
Zn	34.8	15.4

Pb, Ni and V were below detection limits; Hg was not analyzed.

*Raw data for these values are at or very near detection limit.

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